T H E S I S

REACTIONS AMONG THE CARBON

OXIDES, METHANOL AND METHANE

by

R. H. BETTS

Edmonton, Alberta.   April 1, 1943.

Thesis

REACTIONS AMONG THE CARBON
OXIDES, METHANOL AND METHANE

Submitted in Fulfilment

of the

Requirements for the Degree of

Master of Science

by

R. H. BETTS

Under the Direction of

Dr. E. H. Boomer

University of Alberta,
    Edmonton.   April, 1943.

1944
#1

TABLE OF CONTENTS

INTRODUCTION

The development of a chemical industry depends, in general, upon many factors. Among the more important are: an abundant source of cheap raw materials and power; the development of chemical processes to convert these raw materials into products of marketable value; and lastly, the establishment of a market for the manufactured products. The first factor is one for the engineer and geologist; the third factor, one for the economist, while the second factor is one for the chemist and chemical engineer.

In Alberta, there are many sources of cheap raw materials, as for example, the enormous coal deposits, the tar sands of the North, and the oil and gas producing areas of Turner Valley. Each of these await further development, in an economic as well as in a strictly chemical sense. In particular, the large quantities of paraffin hydrocarbons represented by the enormous resources of natural gas in the Province offer an attractive field for exploitation by the chemist.

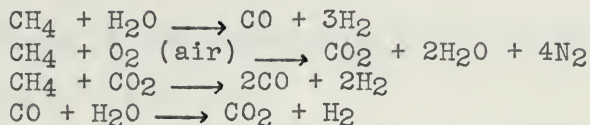A particular field of immediate and urgent interest is the oil and gas producing area of Turner Valley, where large quantities of natural gas are wastefully vented to the atmosphere or burned in flares. At the present time, in excess of a billion cubic feet is wasted each month. Already, some of this gas is being converted into ammonia and associated products at Calgary. Much more gas could be utilized by other

production through well known processes; for example, the manufacture of methanol and its derivatives, derivatives of ammonia, or products resulting from their combination. The interest of the work being reported lies in the development of new processes utilizing the natural gas hydrocarbons or readily prepared primary derivatives of them.

If one can find a process for the direct utilization of the gaseous paraffin hydrocarbons, without the necessity of having to pass through a number of intermediates to reach the desired end product, then obviously this process would be desirable. The paraffins as a class, however, are relatively inert, and offer few such processes. Direct oxidation has been utilized to some extent, especially with respect to the hydrocarbons of higher molecular weight. However, with the lower members of the paraffin family, this method has produced few conspicuous results. Of course, the practice of complete direct oxidation of these materials as a fuel is common. But partial oxidation to alcohols, aldehydes and ketones has in general met with little success. Pyrolysis, i.e., decomposition by heat, has also been investigated in this connection. This method has resulted in production of large quantities of carbon and hydrogen, and certain other products, largely aromatics and olefins, in lesser amounts.

Turning from the direct methods for utilization of the paraffins, one finds more possibilities. The preparation

of hydrogen and the oxides of carbon by interaction of water
and methane under suitable conditions gives the chemist more
reactive materials. The reactions

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$
$$CH_4 + O_2 \text{ (air)} \longrightarrow CO_2 + 2H_2O + 4N_2$$
$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$
$$CO + H_2O \longrightarrow CO_2 + H_2$$

permit the preparation of any desired mixture or pure gas,
and are all operated in one combination or another on an
industrial scale. The production of ammonia by combination
of hydrogen with the nitrogen of the air has already been
mentioned. This ammonia, together with formaldehyde, readily
obtained from methanol, offers endless possibilities in the
field of synthetic polymers. The Fischer-Tropsch synthol
reaction is another means of utilizing carbon monoxide and
hydrogen. Of course, the many uses of carbon dioxide by
itself are not to be overlooked.

This research has been initiated to investigate
further the direct and indirect utilization of methane and
its associated products, carbon monoxide, carbon dioxide and
methanol. The scope of this research has been limited to
an investigation of the catalytic production of acetic acid
from

(1) the direct carbonation of methane

(2) the reactions among methane, oxygen and carbon mon-
oxide, involving the consecutive reactions

$$2CH_4 + O_2 \longrightarrow 2CH_3OH$$
$$CH_3OH + CO \longrightarrow CH_3COOH$$
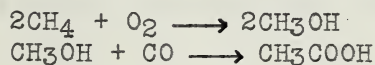
(3) the reaction between carbon monoxide and methanol.

THEORETICAL AND LITERATURE REVIEW

There are many methods available for the study of catalytic reactions. Among the more common are:

(1) the study of the decomposition of the desired products over various catalysts;

(2) an examination of the thermodynamic properties of reactants and products;

(3) direct experimental attempts at the desired synthesis.

Considering the first of these, the theory of simple catalysed reactions states that both forward and reverse reactions are catalysed to the same extent. It follows then, for example, if a catalyst can be found that will split acetic acid into carbon dioxide and methane, or alternatively, into carbon monoxide and methanol, then such a catalyst should promote the appropriate reverse reactions. This method is of some use when little or nothing is known of the type of catalyst required for a given reaction. It will serve in a qualitative way to indicate the nature of the required catalyst, e.g., whether an irreduceable metallic oxide or an acidic oxide is more effective. Thus the development of a process for the synthesis of methanol from hydrogen and carbon monoxide was materially aided by investigations of this type. However, the method is by no means infallible. Indeed, the results obtained from such an investigation may

-4-

be of no practical application whatever. Morris[12], who
used such a method in the attempted synthesis of ethanol
from water gas, concludes that "......... catalysts developed
at atmospheric pressure were not particularly useful, and did
no more than indicate the basic types that might be of use.
.... The only method applicable in the present state of
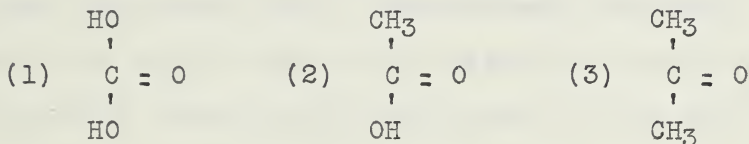the science of catalysis may be described as trial and error."

Again, this method may fail to indicate a synthetic
procedure that would be eminently satisfactory. Thus the
decomposition of acetic acid into methanol and carbon mon-
oxide over phosphoric acid has never been demonstrated, and
yet the synthesis may be achieved fairly readily[9].

The limited value of this method is particularly
evident in the field of heterogeneous catalysis. In general,
one may attribute the poor results to two factors. First
it is rare that reactions are simple and clean-cut. Usually,
a given reacting system can proceed along a number of routes
through both concurrent and consecutive processes, to give
a number of independent products. Thus, though one may
identify certain products formed from the decomposition of
a given compound, that is no guarantee that these same
products may be recombined to give the original compound.
Second, since heterogeneous reactions are dependent on
adsorption at catalyst surfaces, that the simple theory should
hold would be unexpected. To elucidate, a catalyst promoting
A $\longrightarrow$ B would be a good adsorbent for A, and not for B. In

order to promote B ⟶ A, the reverse adsorbtive behaviour
would be advantageous.

The decomposition products of acetic acid have been
reported as carbon dioxide and methane, when the acetic acid
was passed over a reduced nickel catalyst[17]. Other pro-
ducts of decomposition have also been reported. Direct
pyrolysis has yielded carbon monoxide, ethylene, acetic
anhydride and ketene[8]. The familiar reaction of acetic
acid forming acetone, carbon dioxide and water, under in-
fluence of calcium carbonate is encountered frequently[14].
This reaction is used on a commercial scale.

Hurd and Martin[8] have established a theoretical
background to explain the formation of all these end products.
Since the methyl group in the methane system is the analogue
of the hydroxyl group in the water system, the compounds of
methane and water are similar:

$$
(1) \quad
\begin{array}{c}
HO \\
| \\
C = 0 \\
| \\
HO
\end{array}
\qquad
(2) \quad
\begin{array}{c}
CH_3 \\
| \\
C = 0 \\
| \\
OH
\end{array}
\qquad
(3) \quad
\begin{array}{c}
CH_3 \\
| \\
C = 0 \\
| \\
CH_3
\end{array}
$$

Now carbonic acid, (1) above, breaks down into carbon dioxide
and water on heating, while acetone, (3) above, breaks down
into ketene and methane[8]. On this basis, Hurd suggested
that acetic acid, (2) above, considered as a structural
hybrid of carbonic acid and acetone, should break down funda-
mentally into carbon dioxide and methane, or into ketene and
water. This latter reaction has been demonstrated[8].

Moreover, both reactions may proceed simultaneously, with the overall effect of producing acetone, carbon dioxide and water. To account for the carbon monoxide and ethylene, found by Nef[14], Hurd suggested that ketene breaks down to ethylene, and carbon monoxide, according to

$$2C_2H_2O \longrightarrow C_2H_4 + 2CO$$
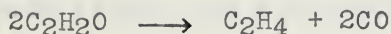
These various possibilities have been confirmed in experiments carried out in this laboratory[1]. Thus it was found that reduceable metallic oxides as nickel oxide, promoted the carbon dioxide-methane reaction, while the basic oxides, e.g., calcium oxide, promoted the acetone-carbon dioxide-water reaction. Irreduceable metallic oxides, e.g., chromium oxide, promoted the ethylene-carbon monoxide reaction. This then serves as an indication of the nature of the catalyst to be used in the direct carbonation of methane.

As for the second method of studying catalytic reactions mentioned above, thermodynamic analysis: this particular application of the method is merely one phase of a principle theoretically applicable to the whole field of chemistry. To successfully apply this method, one requires the following data:

(1) heat capacity equations for the reactants and products

(2) standard heats of formation of reactants and products and

(3) values for the standard free energy of formation for reactants and products. There may be a limitation on this

method due to lack of such data. Inherent in the method itself however, is another limitation. Even with complete thermal data, one cannot say with certainty whether a given reaction will proceed, but merely that it may do so, realization being dependent on existence of a mechanism. Thermal analysis allows the calculation of equilibrium constants for a reaction, but does not predict whether or not equilibrium can be reached, and at what rate. The problem of attainment of equilibrium and rate of reaction is usually a study in mechanisms and catalysis.

The necessary data for the reactions of present interest are listed in Table I.

TABLE I

	$\Delta F(298^{\circ}K)$	$\Delta H(298^{\circ}K)$	C_p
Carbon dioxide	-94,240	-94,030	10.34 + 0.00274 T.
Methane	-12,130	-17,860	5.34 + 0.0115 T.
Carbon monoxide	-32,780	-26,390	6.73 + 0.0012 T.
Methanol	-38,890	-57,230	2.0 + 0.03 T.
Acetic acid	-91,230	-104,700	6.5 + 0.038 T.

These data have been selected from the most recent literature available on the subject[15],[18]. Unfortunately, the heat capacity equation for acetic acid can be regarded as an approximation only, derived empirically from the heat capacity equation for ethanol[15]. The use of this approximate heat capacity equation introduces some uncertainty in

the final expression of the equilibrium constant K as a function of the temperature T, for the reaction. It is unlikely however that the general trend of K as T changes is in error.

For the reaction

$$CO_2 + CH_4 \longrightarrow CH_3COOH,$$

it is found that

$\Delta F_T = +8,200 + 15.05\ T \log T - 6.8\ T - 0.0106T^2$

$\Delta F\ (600^\circ K) = +25,400$ calories

$\log K = \dfrac{-\Delta F}{4.571T} = -9.3$

$\Delta F\ (1000^\circ K) = +46,000$ calories, $\log K = -10.0$

It is obvious from the values of log K that the yield of acetic acid will be very small, and will decrease somewhat with increasing temperatures. Increased pressure will, of course, increase the yield of acetic acid from this reaction. Thus the problem of the preparation of acetic acid from these two components has been narrowed down to a search for an active, low temperature catalyst. This is not promising.

For the reaction

$$CO + CH_3OH \longrightarrow CH_3COOH,$$

$\Delta F_{(T)} = -31,100 - 0.824\ T \log T - 0.775\ T^2 + 40.3\ T$

$\Delta F(300^\circ K) = -26,500 \qquad \log K = 19.3$

$\Delta F(600^\circ K) = -36,200 \qquad \log K = 13.2$

From this equation, and the values of log K, it is seen that yield of acetic acid will be large, approaching 100% at equilibrium. Other reactions such as dehydration or

decomposition to carbon monoxide and hydrogen of methanol, and the production of carbon dioxide and carbon from carbon monoxide are likely to occur. The concurrent reactions are either unaffected or are repressed by high pressures, and the use of such pressures is indicated in this reaction.
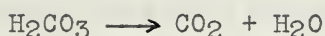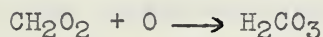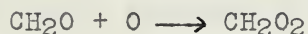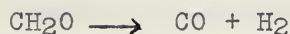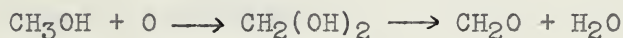
From thermodynamic considerations alone, the successful preparation of acetic acid from carbon dioxide and methane appears doubtful, while its preparation from carbon monoxide and methanol appears more favourable.

Proceeding to the third method of catalytic investigation mentioned above, that of direct experimental attempts at the desired synthesis: while this method may make intelligent use of the results obtained from methods (1) and (2) above, it cannot at the present time be other than an empirical catalyst search. This method provides the ultimate test for any theoretical conclusions derived from other sources. Moreover this method, as Krase and Singh[9] state, "........ required multiplicity of manpower and testing equipment."

The literature on the production of acetic acid from carbon dioxide and methane is confined almost exclusively to patents. A typical patent is one of Dreyfus[3] who claims a temperature of 300°C - 500°C, 10-200 Kg. pressure, and the presence of an oxide, hydrate, carbonate, bicarbonate or phosphate of an acidic metal oxide, for the production of acetic acid from carbon dioxide and methane. However,

B. Maldowski[11] carried out experiments, with results
confirming thermodynamic calculations, showing that these
patents were unworkable.

It has been shown[2] that appreciable yields of
methanol may be obtained by the direct oxidation of methane
over copper catalysts at elevated temperatures and pres-
sures. The mechanism of the oxidation of methane has been
explained[2] as a successive introduction of oxygen atoms
into the methane molecule:

$$CH_4 + O \longrightarrow CH_3OH$$
$$CH_3OH + O \longrightarrow CH_2(OH)_2 \longrightarrow CH_2O + H_2O$$
$$CH_2O \longrightarrow CO + H_2$$
$$CH_2O + O \longrightarrow CH_2O_2$$
$$CH_2O_2 + O \longrightarrow H_2CO_3$$
$$H_2CO_3 \longrightarrow CO_2 + H_2O$$

While the parent compound is very resistant to oxidation, the
succeeding compounds are readily attacked by oxygen. More-
over these compounds are thermo-labile, and decompose into
hydrogen, carbon monoxide and water as indicated above.
Indeed, when one oxygen atom has been introduced into the
methane molecule, the successive reactions of oxidation and
decomposition proceed so rapidly that the end products of
oxidation of methane are usually carbon dioxide and water.

If, in some way, the primary product could be
removed from the oxidation zone (the surface of the copper)
before further reaction could occur, this method would offer

an attractive means for utilization of methane. An alternative to this rapid removal would be to convert the readily oxidizable methanol into another product, more resistant to oxidation. Such a product is acetic acid. This compound has a high degree of thermal stability, and its structure is extremely resistant to oxidation.

The addition of carbon monoxide to a suitable mixture of methane and oxygen offers, at least theoretically, a possibility for indirect carbonation of methane to acetic acid, by means of the consecutive reactions

$$CH_4 + O \longrightarrow CH_3OH$$
$$CH_3OH + CO \longrightarrow CH_3COOH$$

In any event, it is a matter of some interest to determine the extent of the oxidation reaction in the presence of various concentrations of carbon monoxide, e.g., whether the carbon monoxide will be attacked exclusively, or in particular, whether the successive reaction of oxidation to methanol and carbonation to acetic acid will go.

The indirect carbonation of methane to acetic acid has been accomplished by Grignard[5], who proceeded from methane through methyl bromide by halogenation, to methyl magnesium bromide (a Grignard reagent). An ethereal solution of this reagent was allowed to drop onto dry ice (solid carbon dioxide). In a matter of seconds, the following reaction occurred:

$$CH_3MgBr + CO_2 \longrightarrow CH_3CO_2MgBr.$$

When this material was hydrolyzed, the original methyl bromide
was converted almost quantitatively into acetic acid:

$$CH_3CO_2MgBr + H_2O \longrightarrow CH_3COOH + MgOHBr$$

However, it would be impractical to use this method on a
commercial scale.

The synthesis of acetic acid from carbon monoxide
and methanol has been reported several times in the litera-
ture. Hardy[6], using a catalyst of 87% phosphoric acid and
2% copper phosphate, found under optimum conditions of his
apparatus, that 44.9% of the methanol was converted to acetic
acid or methyl acetate, 9.5% to dimethyl ether, 4.8% to free
carbon, 5.0% loss and 35.8% unchanged. He used a recircula-
tion assembly, in which carbon monoxide was passed through
methanol and the saturated vapours then passed through the
catalyst. However, maximum conversion of carbon monoxide to
acetic acid per pass was found to 0.5%. He also reports
that as the carbon monoxide:methanol ratio dropped from
40:1 to 10:1, the total yield of acid dropped to 3%. Hardy
also suggests that dimethyl ether is an intermediate in the
production of acetic acid in this process. Singh and
Krase[9] have also investigated this reaction, using as a
catalyst, charcoal impregnated with phosphoric acid. Using
a one pass system, considerable quantities of dimethyl ether
were formed, up to 90% of the methanol delivered to the
catalyst being so converted. A maximum yield of 10.0%
acetic acid, based on amount of methanol delivered to the

catalyst, was obtained. The use of a recirculation system, in which the off-gases were not expanded, but recirculated over the catalyst, together with more methanol, increased the yield of acetic acid up to 36%, with a corresponding decrease in dimethyl ether production. The carbon monoxide: methanol ratio was of the order of 40:1. These workers also suggest that dimethyl ether is an intermediate in the formation of acetic acid.

Earlier work done by these same men[9] in which carbon monoxide was bubbled through liquid methanol in presence of various catalysts, gave no acetic acid whatever. They concluded that any further work to be done on this reaction should be limited to vapour phase studies.

The patent literature contains many references to the production of acetic acid by this reaction. The list of catalysts is extensive and covers a multitude of compounds and elements, as for example, oxides of titanium, aluminum, silicon, copper oxide, lead oxide, sulfonic acids, bismuth, thorium, etc. However, these claims are of little interest, since they are not accompanied by experimental results.

The investigations outlined in this report have included all three possibilities discussed above. The experimental material will be divided into three parts:

PART I

The direct carbonation of methane to acetic acid.

PART II

The preparation of acetic acid by means of the consecutive reactions

$$CH_4 + O \longrightarrow CH_3OH$$
$$CH_3OH + CO \longrightarrow CH_3COOH$$
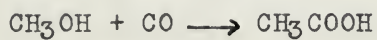
PART III

The preparation of acetic acid from methanol and carbon monoxide.

CARBON DIOXIDE - METHANE REACTION

Experimental Methods

Materials -

Carbon dioxide was obtained from a cylinder of commercial liquid carbon dioxide, and was used without further purification. The methane used was Viking natural gas, freed from sulfur added as an odorant, by passage over activated charcoal before compression. Some of the higher molecular weight hydrocarbons were also removed by the charcoal. This gas was analyzed by low temperature fractional distillation[4], and had the following composition:

> 93.1% methane
>
> 4.7% nitrogen
>
> 1.7% ethane
>
> 0.5% propane and higher

Many catalysts were tested in this work. Typical of these are: (numbers are given with reference to Table II below)

Catalyst 1.- Reduced nickel oxide. The catalyst was prepared by roasting the nitrate in presence of porcelain chips as a carrier. Activation was secured by reduction with hydrogen at 300°C.

Catalyst 2.- Zinc and chromium oxides in equimolar

amounts. This catalyst was prepared by coprecipitation of the respective hydroxides. These hydroxides were washed free of sodium nitrate, and dried at 120°C for one day.

Catalyst 14.- Palladium on asbestos. This catalyst was prepared by precipitation of palladium from a palladium chloride solution on long fibre asbestos. It was activated by treatment with hydrogen at 300°C.

Catalyst 15.- Platinum on asbestos. This catalyst was prepared from a platinum chloride solution, by reduction of the platinum ion with formalin solution. The metal was precipitated onto the carrier. It was ignited, and activated with hydrogen at 350°C.

Catalyst 18A.- Cobalt on charcoal. This catalyst was prepared by the precipitation of the hydroxide from a solution of the nitrate salt, in the presence of activated charcoal as a carrier. The hydroxide was dried at 130°C for one day before use.

Catalyst 21.- Zinc ferrate. This catalyst was prepared by fusion of a mixture of zinc sulfate, sodium sulfate and ferric sulfate, followed by extraction of the melt with dilute acetic acid. The zinc ferrate, being feebly ferromagnetic, was purified by electromagnetic concentration.

Catalyst 23.- An equimolar mixture of iron, cobalt and nickel oxides. It was prepared by coprecipitation of the metals as their hydroxides, in the presence of a charcoal

carrier. The oxides were formed by dehydration, and were activated at 300°C with hydrogen.

Catalyst 28.- A Hopcalite type catalyst. It was prepared from cobalt sulfate, after the method of Merrill and Scalione[10].

This list is incomplete, but it serves to indicate the variety of catalysts tested in this investigation.

Apparatus

The apparatus, which is shown in figures 1 and 2, consisted essentially of a means for passing carbon dioxide-methane mixtures, at suitable pressure and rate of flow, over a catalyst bed maintained at any desired temperature.

Figure 1 gives the essential parts of the apparatus. A high pressure storage vessel, A, was connected to a three stage compressor through the valve C. The Bourdon gauge, M, previously calibrated by comparison with a deadweight piston gauge, indicated the pressure. The reaction system was connected with the storage system through valve N. This reaction system consisted of a reaction vessel, figure 2, (the details of which are given below), followed by a high pressure bronze condenser D. The condenser was followed by the expansion valve E, placed in a heated oil bath as shown. An atmospheric pressure spiral condenser F, followed the expansion valve. It was kept immersed in an ice-water mixture. The off-gas flow rate was indicated by the flow meter G. This rate could be adjusted by means of the expansion valve. A continuous proportional sampler, indicated at H, was used in taking a sample of the off-gas. The confining liquid in this device was a solution of 20% sodium sulfate, 5% sulfuric acid and 75% water. Such a solution will not dissolve significant amounts of the components of the off-gas. The volume of gas was measured in the calibrated

System for CO_2 + CH_4 reaction.
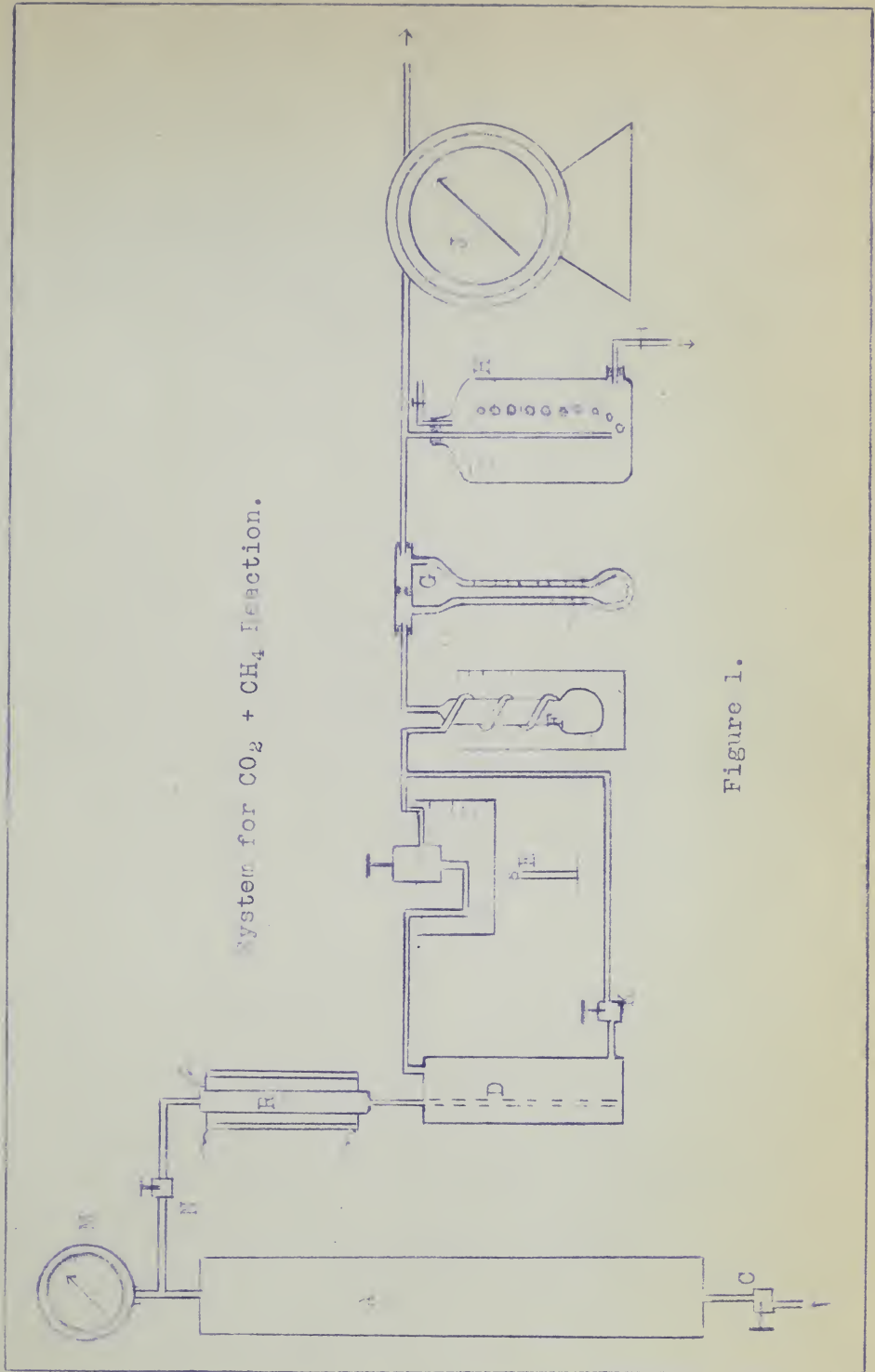
Figure 1.

wet-test meter J. Any liquid that might accumulate in the
condenser D, could be blown off into the low pressure con-
denser F, by opening valve K.

The details of the reaction vessel are shown in
figure 2. It consisted essentially of a stainless steel
tube A, 9" x 7/8" O.D. x $\frac{1}{4}$" I.D. This reactor had a volume
of 7.6 c.c. The catalyst was held in place in the reactor
by means of discs of copper mesh. This tube was enclosed
in a cast iron pipe B, and surrounded by a lead bath C. The
bath was heated by means of resistance wire wound over
asbestos sheet sheathing the pipe B. An outer layer of
asbestos cement provided heat insulation. A thermocouple
well D, immersed in the lead bath, contained a calibrated
iron-constantan thermocouple. The temperature was maintained
manually by the adjustment of resistances in the heating
circuit, and could be controlled to $\pm$ 5°C. This reactor
could be used safely at 450°C, with internal pressures up to
3800 p.s.i.

To prepare the gas mixture, a cylinder of liquid
carbon dioxide was attached to the storage system through
the valve C. After the carbon dioxide had expanded into A,
up to its vapour pressure, (ca. 800 p.s.i.), the cylinder
was disconnected. Valve C was then connected to a line
from the compressor, and methane was pumped into A. By this
means, a homogeneous mixture of the two gases was readily
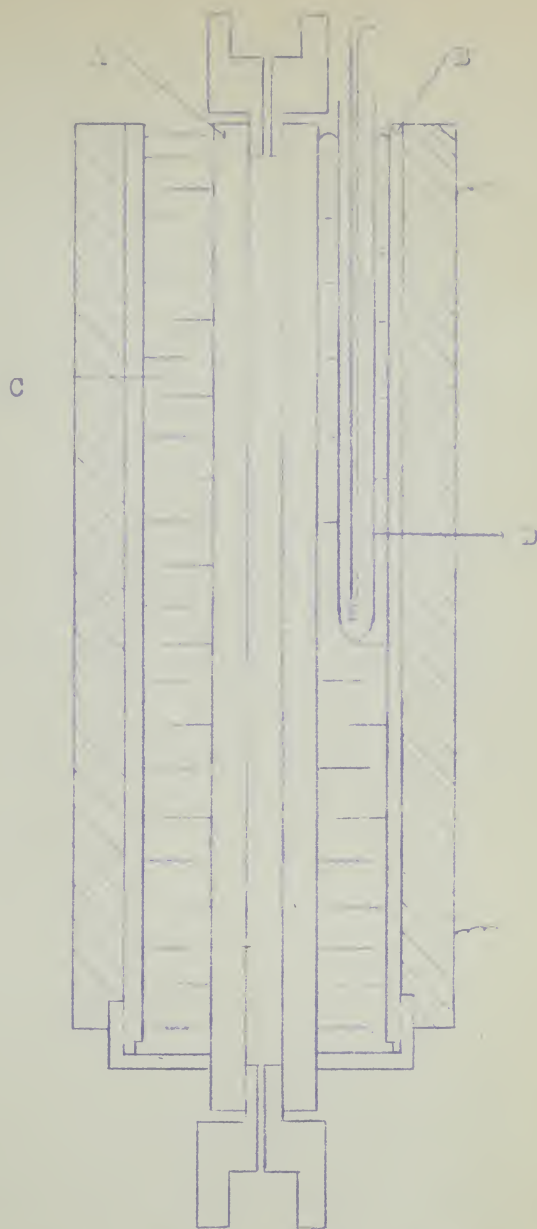obtained. Moreover, this method allowed the utilization of

Figure 2. High Pressure Reactor.

high pressures, much above that of the vapour pressure of carbon dioxide. By this means, mixtures containing from 50% to 80% methane were obtained. The exact percent of methane depended upon the final pressure attained.

The operating procedure was relatively simple. After the catalyst bed had attained the proper temperature, valve N (figure 1) was opened, and the carbon dioxide - methane mixture entered the reactor and the condenser. The expansion valve E was now opened, and the rate of off-gas flow was adjusted by reference to the flow meter G. After the expansion train had been thoroughly swept out, the continuous proportional sampler was started. The off-gas volume was determined by readings of the wet-test meter J. At the conclusion of the run, the contents of condenser D were blown off into the low pressure condenser F, through valve K. The pressure drop during a run was between fifty and one hundred pounds p.s.i.

Analytical Methods

Off-gas analyses were carried out in duplicate in an improved type of Bureau of Mines Orsat apparatus. Carbon dioxide was determined by absorption in aqueous potassium hydroxide, oxygen in aqueous alkaline pyrogallate solution, hydrogen and carbon monoxide by combustion over copper oxide. Methane was determined by slow combustion with oxygen on a platinum filament. Nitrogen was determined by difference.

Results

The results for a representative group of runs are tabulated in Table II.

TABLE II

Run No.	1	5	22	24	31	35
Catalyst	None	2	15	17	23	18A
Temperature $^{o}C.$	355	395	450	450	450	500
Pressure,p.s.i.	800	1350	1850	1650	3675	Atm.
Space Velocity	42	60	100	120	Varied	Varied
In-Gas:						
CO_2 %	44.6	46.5	17.10	24.0	23.20	23.20
$CH_4 + N_2$	55.4	53.5	82.90	76.0	76.80	76.80
Off-Gas:						
(Volume cu.ft.) (at N.T.P.)	0.20	1.32	3.05	4.60	2.74	2.69
CO_2	44.6	46.5	17.10	23.80	23.15	20.40
H_2	-	-	-	0.14	0.17	1.67
CO	-	-	-	-	-	1.31
$CH_4 + N_2$	55.4	53.5	82.90	76.00	76.70	76.60
Condensate	0	0	0	0	0	0

The space velocity is expressed as number of c.c. of off-gas, measured at N.T.P., per c.c. of catalyst volume, per minute.

Run 35 was carried out at atmospheric pressure, to

determine the activity of this catalyst for the reactions

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$

$$2CO \longrightarrow CO_2 + C$$
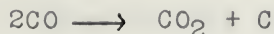
As is seen, appreciable amounts of hydrogen were formed. The catalyst (cobalt on charcoal) was found to be pyrophoric at the end of the run. This catalyst appears to be relatively active in promoting the first of the above reactions. However, this catalyst while able to promote reactions between carbon dioxide and methane, was not effective in opening the methane molecule sufficiently to allow it to react with carbon dioxide to form acetic acid.

These negative results, while disappointing, are not unexpected in view of the known inactivity of methane, and also in view of the thermodynamic properties of the reaction, as described above. Any further attempts to demonstrate the direct carbonation of methane may lie in the use of much higher pressures, and more highly active catalysts useful at lower temperatures. Certainly, under the conditions used in this work, direct carbonation of methane may be considered unlikely.

PART II

REACTIONS AMONG CARBON MONOXIDE, METHANE AND OXYGEN

Experimental Methods

Materials -

Viking natural gas, treated as described in Part I, of composition given on page 16, was taken as the supply of methane. Compressed oxygen as supplied commercially was used without further purification.

Carbon monoxide was prepared from practical grade formic acid by dehydration with syrupy phosphoric acid:

$$HCOOH \longrightarrow CO + H_2O$$
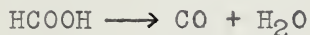
Phosphoric acid was used instead of sulfuric acid to prevent charring of the formic acid. Formic acid was dropped into boiling 85% phosphoric acid, and the resulting water and carbon monoxide were immediately distilled out of solution. Most of the water vapour was removed in a water cooled condenser. The carbon monoxide was washed with aqueous potassium hydroxide solution to remove any carbon dioxide that may have been formed in the dehydration step. The resulting gas was pure carbon monoxide, and was stored until required in a water-sealed gas-holder.

Required mixtures of the gases were made by carefully metering the individual gases through a wet-test meter into a water-sealed gas-holder. To hasten the natural processes of diffusion, these gases were added to the gas

holder in the order of increasing density. The resulting
mixture was allowed to stand until it was found to be
homogeneous.

The catalyst used in these experiments was metallic
copper in the form of short lengths of heavy wire of dimen-
sions 2.5 cm long, 0.16 cm diameter. The total mass of the
copper was 118.0 grams. The volume occupied by the catalyst
in the reactor, including free space, was 30 cubic centi-
meters.

Apparatus

The apparatus, shown in figure 3, was relatively simple. Gas entered the reaction system from storage vessel A, through valve D. The reaction chamber, E, consisted of a tube of high nickel-chromium steel, with a copper lining extending over its sides and ends. This chamber was maintained at the desired temperature by means of a split multiple unit electrical furnace F. Even distribution of temperature throughout the length of the chamber was obtained by means of a split brass cylindrical jacket, G, placed between the reaction chamber and the heating elements. The temperature was determined by means of a calibrated iron-constantan thermocouple, inserted in a groove cut in the inner surface of the brass cylinder, and exposed to the wall of the reaction chamber. The temperature was controlled by means of appropriate rheostats and a recording potentiometer controller. Temperatures were maintained constant to $\pm 2^{\circ}C$.

From the reactor, a line led to the bottom of a water cooled high pressure condenser, J. The off-gases left the condenser through an overhead take off, and were passed through a heated expansion valve, K, into the condenser train. This condenser train consisted of a spiral glass condenser, L, which was immersed in an ice-water mixture. The condenser was followed by a flow meter, M.

System for Reaction Among CO + O₂ + Cl₄.
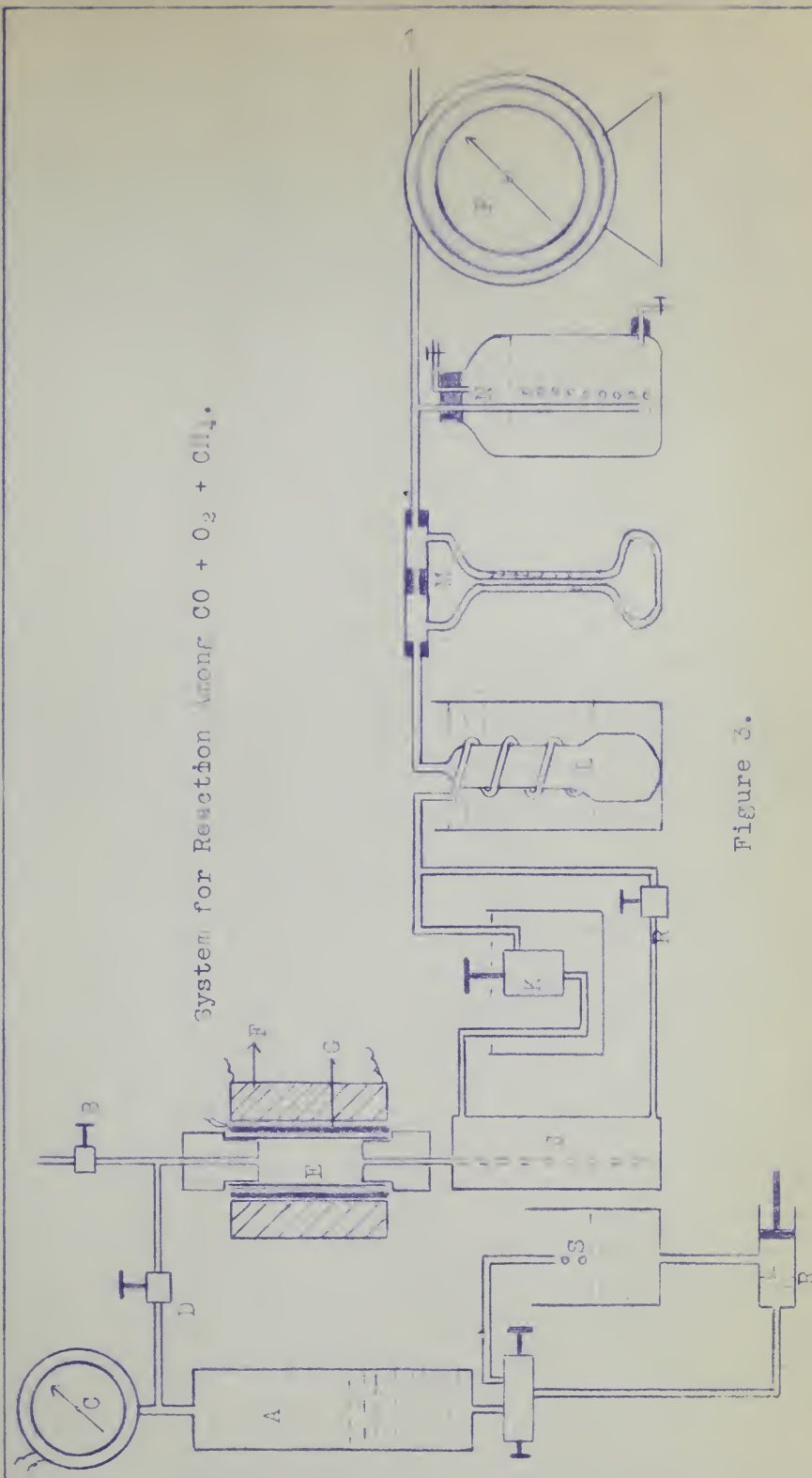
Figure 3.

A continuous proportional sampling device, N, and a calibrated wet-test meter, P, completed the expansion train.

The pressure control system merits some description (figure 3). A 50% glycerine-water mixture was pumped into vessel A by means of the hydraulic pump R. This liquid served as a hydraulic piston for the compression of the gas in A up to the operating pressure. This glycerine-water mixture had no corrosive action on the metal parts of the apparatus. Moreover, it did not dissolve serious amounts of the gas mixture. A Bourdon gauge, C, previously calibrated by comparison with a dead weight piston gauge, indicated the operating pressure. Two contacts, high and low, on the gauge C, operating through a relay, controlled a light. As gas was withdrawn through valve D, to the reaction system, the movement of the gauge index operated the light, which was the visual signal for the operator to start the hydraulic pump. As the glycerine-water was pumped into vessel A from reservoir S, the pressure rose. When it reached the required operating pressure, the light was automatically turned off. This was the signal to stop the pump. By this means, pressure in the reactor was maintained within one or two atmospheres.

The initial charge of gas to vessel A was obtained from the gas-holder containing the gas mixture by use of a three stage compressor.

Operating Procedure

The gas pressure in the storage vessel A was built up by injection of glycerine-water solution with the hydraulic pump to 200 p.s.i. above that desired for a run. When the temperature of the reactor had reached the desired value, valve D was opened. This allowed the gas mixture to enter the reactor and high pressure condenser. The pressure control apparatus described above was then set. The expansion valve, K, was adjusted to permit the desired rate off-gas flow as indicated by the flow meter, M. After 5-10 litres of gas had passed and flushed the expansion train, the continuous proportional gas sampling device was started. At the conclusion of the run, valve A was closed, the sampling device shut off, and the residual gas left in the reactor and condenser were allowed to expand through the expansion train. Any liquid products formed in the reactor and retained in the high pressure condenser J, were blown over into the glass condenser L by cautiously opening valve R. The volume of off-gas was determined by the wet-test meter, (plus the volume in the sampling device). The quantity of liquid products formed was measured by the increase in weight of the condenser L.

Analytical Methods

The analyses of in-gas and off-gas were made in duplicate, using an improved type of Bureau of Mines Orsat apparatus described in Part I.

The liquid condensate was examined for acids, formaldehyde and methanol. An excess of standard alkali was added to an aliquot portion of the liquid, and this solution was boiled to remove any carbon dioxide. This was followed by back titration with standard sulfuric acid with phenolphthalein as the indicator. Formaldehyde was tested for qualitatively, using Schiff's fuchsin-aldehyde reagent. Methanol was tested for by careful fractional distillation of the liquid in a 20 cm. vacuum jacketed fractionating column. This method could not be used in a quantitative manner, but it served to indicate the presence or absence of liquids with boiling points corresponding to that of methanol.

Experimental Results

Thomas[19] has found that the operating pressure
and temperature have profound effects upon the end products
of direct oxidation of methane. The optimum conditions of
temperature and pressure for the formation of methanol by
this reaction found by Thomas have been used in this investi-
gation. These conditions are

(1)   an operating temperature of 400°C,

(2)   a pressure between 2000-2100 p.s.i.

It is realized that such a procedure is open to criticism,
since in this work we are concerned not merely with oxygen
and methane, but with oxygen, methane, and carbon monoxide.
However, as a first approximation, it was felt that these
conditions, in the absence of other data, were those most
liable to produce positive results.

The consistency of the results was checked by means
of material balances. Thomas[19] has investigated this
method, and concluded that carbon balances in particular are
quite reliable.

The method may be described as follows: the total
carbon content of the off-products is found. From this
quantity, and the analysis of the in-gas, the volume of the
in-gas which had entered the reactor may be calculated.
When the volume of the in-gas is calculated, this figure can
be used in determining the balance between the in-hydrogen,

and off-hydrogen. Similar calculations can be applied to the nitrogen and the oxygen. The difference between these figures is a measure of the accuracy of one's analytical methods. However it may be noted that oxygen balances obtained in this way are frequently poor, and discrepancies greater than any possible analytical error may exist. No satisfactory explanation has been found[13].

The method will be illustrated in detail using the data of Run 9, as listed in Table III.

Sample calculation.-

Off-gas analysis:

$$
\begin{aligned}
\text{Volume} &- 117.3 \text{ l. N.T.P.} \\
CO_2 &= 4.65\% \\
O_2 &= 0.42\% \\
H_2 &= 0.12\% \\
CO &= 1.62\% \\
CH_4 &= 88.50\% \\
N_2 &= 4.69\%
\end{aligned}
$$

Condensate 2.84 grams, found to be water.

$$C \text{ in } CO_2 = \frac{0.0465 \times 117.3 \times 12.0}{22.4} = 2.93 \text{ grams}$$

$$C \text{ in } CO = \frac{0.0162 \times 117.3 \times 12.0}{22.4} = 1.02 \text{ grams}$$

$$C \text{ in } CH_4 = \frac{0.8850 \times 117.3 \times 12.0}{22.4} = 55.60 \text{ grams}$$

Total carbon in off-gas	=	59.55 grams
Carbon in condensate	=	0.00
Total carbon	=	59.55 grams

In-gas analysis:

$$CO_2 = 0.0\%$$

$$O_2 = 5.15\%$$

$$H_2 = 0.0\%$$

$$CO = 5.15\%$$

$$CH_4 = 85.20\%$$

$$N_2 = 4.50\%$$

Let the volume of the inlet gas be W litres at N.T.P.

Carbon in 0.0515 W litres of CO = $\dfrac{0.0515W}{22.4}$ x 12 = 0.0276W grams

Carbon in 0.8520 W litres of CH_4 = $\dfrac{0.8520W}{22.4}$ x 12 = 0.456W grams

Therefore total carbon into reactor = 0.4836W grams

But carbon into reactor = carbon out of reactor

Therefore 59.55 = 0.4836W

$W = \dfrac{59.55}{0.4836}$ = 123.2 litres, N.T.P.

Using this figure of 123.2 as the volume of the inlet gas, one can calculate the number of grams of hydrogen, oxygen and nitrogen in the in-gas, and compare these values with the corresponding figures for off-gas, plus condensate.

Oxygen balance.-

In-gas:

Grams of elementary oxygen = 0.0515 x $\dfrac{123.4}{22.4}$ x 32 = 9.08 grams

Grams of oxygen in carbon monoxide = 0.0515 x $\dfrac{123.4}{22.4}$ x 16 = 4.54 grams

Total oxygen in = 13.62 grams

Off-gas:

Grams of elementary oxygen $= 0.0042 \times \dfrac{117.3}{22.4} \times 32 = 0.70$ grams

Grams of oxygen in carbon dioxide $= 0.0465 \times \dfrac{117.3}{22.4} \times 32 = 7.83$ grams

Grams of oxygen in carbon monoxide $= 0.0162 \times \dfrac{117.3}{22.4} \times 16 = 1.37$ grams

Grams of oxygen in 2.84 grams water $= 2.84 \times \dfrac{16}{18} = 2.52$ grams

Total oxygen accounted for $= 12.42$ grams

Corresponding figures for nitrogen are:

nitrogen in $= 6.94$ grams

nitrogen out $= 6.90$ grams

The hydrogen balance is also good:

hydrogen in $= 18.85$ grams

hydrogen out $= 18.68$ grams

Such close agreement in the material balance obtained by using carbon as the equating element gives one confidence in the use of this method in the interpretation of results. The agreement in the material balance for run 11 is of the same order as that for run 9. Run 10 does not show such close agreement, but the run may be considered significant. The data for these runs are presented in Table III.

Discussion of Results

In run 9, a high concentration of methane, together with low and equimolar concentrations of oxygen and carbon monoxide (5.15%), resulted in the following reactions

TABLE III

Run No.	9	10	11
Temperature °C.	400	400	400
Pressure, p.s.i.	2000	2150	2000
Off-gas flow rate, litres per minute	0.53	0.52	0.54
In-gas:			
Computed Volume in litres, N.T.P.	123.4	125.8	106.5
CO_2	-	0.17	0.13
O_2	5.15	3.14	4.03
H_2	0	1.07	0.69
CO	5.15	48.55	31.05
CH_4	85.20	44.72	60.90
N_2	4.50	2.35	3.20
Off-gas:			
Volume in litres, N.T.P.	117.3	122.0	102.2
CO_2	4.65	5.50	5.93
O_2	0.42	1.40	0.92
H_2	0.12	1.00	0.60
CO	1.62	35.30	25.51
CH_4	88.50	53.90	63.71
N_2	4.69	2.90	3.34
Condensate, grams	2.84	0.0	0.0

occurring:

$$2CO + O_2 \longrightarrow 2CO_2$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
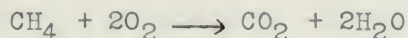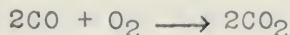
The oxidation reactions continued until practically all available gaseous oxygen was consumed. There was no evidence of oxygenated carbon compounds in the condensate.

In run 10, the concentration of carbon monoxide was increased to 48.5%, the oxygen was held at 3.1%, while the methane was 44.7%. Under these conditions, only one reaction occurred:

$$2CO + O_2 \longrightarrow 2CO_2$$
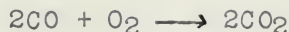
The oxidation of carbon monoxide proceeded until the concentration of oxygen reached 1.4%, and no methane was oxidized.

In run 11, the concentrations of carbon monoxide and methane were midway between the values for runs 9 and 10. The carbon monoxide concentration was 31.0%, methane concentration 60.9%, while the oxygen remained at 4.0%. Even with this richer mixture in terms of methane, only carbon monoxide was attacked. The oxidation of carbon monoxide to carbon dioxide continued until the oxygen concentration reached the value of 0.9%.

Conclusions

Under the conditions of these experiments, the oxidation of carbon monoxide by gaseous oxygen is very much more rapid than the oxidation of methane, so much so that no methane is oxidized when its partial pressure is twice

that of carbon monoxide. When the partial pressure of methane
is about seventeenfold that of carbon monoxide (experiment 9),
methane shares the oxygen with carbon monoxide and oxidation
of both proceeds. In this latter experiment, there was no
trace of methanol formation, a result not at first sight
consistent with the work of Thomas[19].

The inhibition of the oxidation of methane may be
looked upon as a type of selective poisoning of the copper
catalyst. Carbon monoxide is strongly adsorbed by the
copper. The surface of the catalyst becomes completely
covered with these molecules, and any methane molecules that
may strike the surface are not oxidized. However, oxygen
will attack the adsorbed carbon monoxide. As the concentra-
tion of the latter gas is decreased, until comparable with
that of the oxygen, adsorption of oxygen can take place.
Consequently, simultaneous with carbon monoxide oxidation,
methane is oxidized by the oxygen present on the copper
surface. Due to the relative inertness of the methane
molecule to oxidation, it is not expected that every collision
with the adsorbed oxygen will result in reaction. On the
other hand, it may be expected that nearly every collision
of a carbon monoxide molecule with the catalyst surface will
be followed by either adsorption or oxidation. The absence
of methanol formation can be attributed at this time only to
unknown factors such as different properties of the catalyst
surface from those existing in Thomas'[19] experiments.

The preparation of acetic acid by this method is dependent upon the oxidation of methane to methanol over the copper surface, followed by the action of carbon monoxide on the methanol so formed. Evidently the amount of methanol obtained is not sufficient to allow the carbon monoxide-methanol reaction to occur at all. The kinetics of the consecutive reaction require that before the methanol molecule is completely oxidized to carbon dioxide and water, it must meet and react with a carbon monoxide molecule. The probability of this second reaction occurring is very small, when the methanol concentration is practically zero.

Further work on this problem would involve the development of a multiple catalyst that would promote oxidation of methane to methanol, and at the same time promote the carbon monoxide methanol reaction. One important criterion of such a catalyst is that it does not adsorb carbon monoxide, but does adsorb oxygen or methane strongly. The ratio of methane to carbon monoxide must be high, before the first stage of the reaction occurs at all. Further studies in this region are indicated.

THE REACTION BETWEEN CARBON MONOXIDE AND METHANOL

Experimental Methods

Materials -

Carbon monoxide used was prepared from formic acid by the method described in Part II. The gas used in these experiments was not in general pure. The carbon monoxide-rich off-gas was collected after each run, added to the carbon monoxide gas holder, and used over again. Carbon dioxide was removed from this gas by scrubbing with aqueous potassium hydroxide, but hydrogen and methane accumulated gradually. When the concentration of hydrogen and methane together rose above 10%, the gas was discarded, and a fresh supply was made. It is realized that such a procedure may lead to ambiguous results. While methane may be considered inert in these reactions, hydrogen and carbon monoxide may react to produce methanol or methane. In either event, the effects are not of major importance.

The methanol used was prepared from analytical grade acetone-free material by fractional distillation. That fraction boiling between $64.4^{\circ}C$ and $64.6^{\circ}C$ was retained. This methanol had a density of 0.7930 at $20^{\circ}C$, (I.C.T. gives 0.7928). The aqueous solutions of methanol used in several runs were prepared gravimetrically from the above methanol and distilled water.

The acetic acid used in several experiments, and in the standardization of the analytical procedure was analytical grade, assaying 99.5% acetic acid. It was used without further purification. The methyl acetate used in some of the runs, and also in the standardization of the recovery procedures, was also reagent grade. It contained no titratable acid. It was used without further purification.
Catalysts -

Catalyst 1B - calcium phosphate. A solution of calcium nitrate was added to a solution of sodium phosphate. The precipitated material was washed free of nitrate ion by decantation, filtered and dried at 120°C.

Catalyst 2B - 5 calcium phosphate, 1 uranyl biphosphate mixture. This catalyst was prepared by the incorporation of the requisite amount of uranyl nitrate into a moist precipitate of calcium phosphate. The uranyl ion was precipitated as the biphosphate by the addition of an excess of potassium monohydrogen phosphate. The mass was washed free of nitrate ion, filtered and dried at 120°C. This catalyst formed a hard cake that could be broken up and screened to suitable size.

Catalyst 3B - Phosphoric acid and copper phosphate on activated coconut charcoal. This catalyst was prepared by soaking the charcoal in 100 c.c. of syrupy phosphoric acid, to which 3.6 grams of copper phosphate had been added. The charcoal was allowed to remain in contact with the acid solution for one week before use.

Catalyst 7B - Phosphomolybdic acid on an artificial clay as a carrier. This catalyst was prepared by soaking the carrier in a saturated solution of the acid. The mixture was filtered, washed sparingly, and dried at 130°C. The carrier was prepared from sodium silicate and aluminum sulfate. It had a composition represented by the formula $Al_2O_3.2SiO_2$.

Catalyst 8B - Phosphomolybdic and phosphoric acids on pumice stone. This catalyst was prepared by soaking pumice stone in syrupy phosphoric acid. A saturated solution of the second acid was then added, and the mixture was taken to dryness at 130°C. Actually, the phosphoric acid was not dehydrated at this temperature. Consequently, the catalyst surface remained moist.

Catalyst 9B - Activated alumina. This catalyst was 4-8 mesh size alumina as commercially available. It was activated at 200°C for four hours.

Catalyst 10B - Phosphomolybdic acid with activated alumina as a carrier. This catalyst was prepared by soaking activated alumina (from catalyst 9B) in an aqueous saturated solution of the acid. This solution was evaporated to dryness at 130°C. This catalyst proved to be superior to the other phosphomolybdic acid preparations in mechanical properties. It did not disintegrate appreciably during use.

Apparatus and Operation

Two methods were used in this investigation. In the first, carbon monoxide and methanol were mixed in a pre-heater, and then passed over the catalyst. The liquid products were collected in a condenser, and the residual carbon monoxide, together with other gaseous products formed in the reaction, were expanded to atmospheric pressure through a suitable expansion train. The apparatus used in this procedure is shown in figures 4 and 5. In the second method, the off-gases from the condenser were not expanded, but were recirculated over the catalyst by means that will be described below. This apparatus is shown diagramatically in figure 7.

Figure 4 shows the storage system and reactor for the single pass method. Carbon monoxide entered the system from a line connected at valve R. It was compressed in a two stage compressor into the storage cylinder B. A 50% glycerine-water mixture could be pumped into this cylinder from vessel E by means of the hydraulic pump F. Gas pressure in this cylinder was indicated by the Bourdon gauge A. This gauge had been previously calibrated by a dead weight piston gauge. Valve S controlled the flow of carbon monoxide into the preheater H. A check valve G in the carbon monoxide line prevented any gases formed in the preheater or in the reactor from entering the carbon monoxide storage vessel.
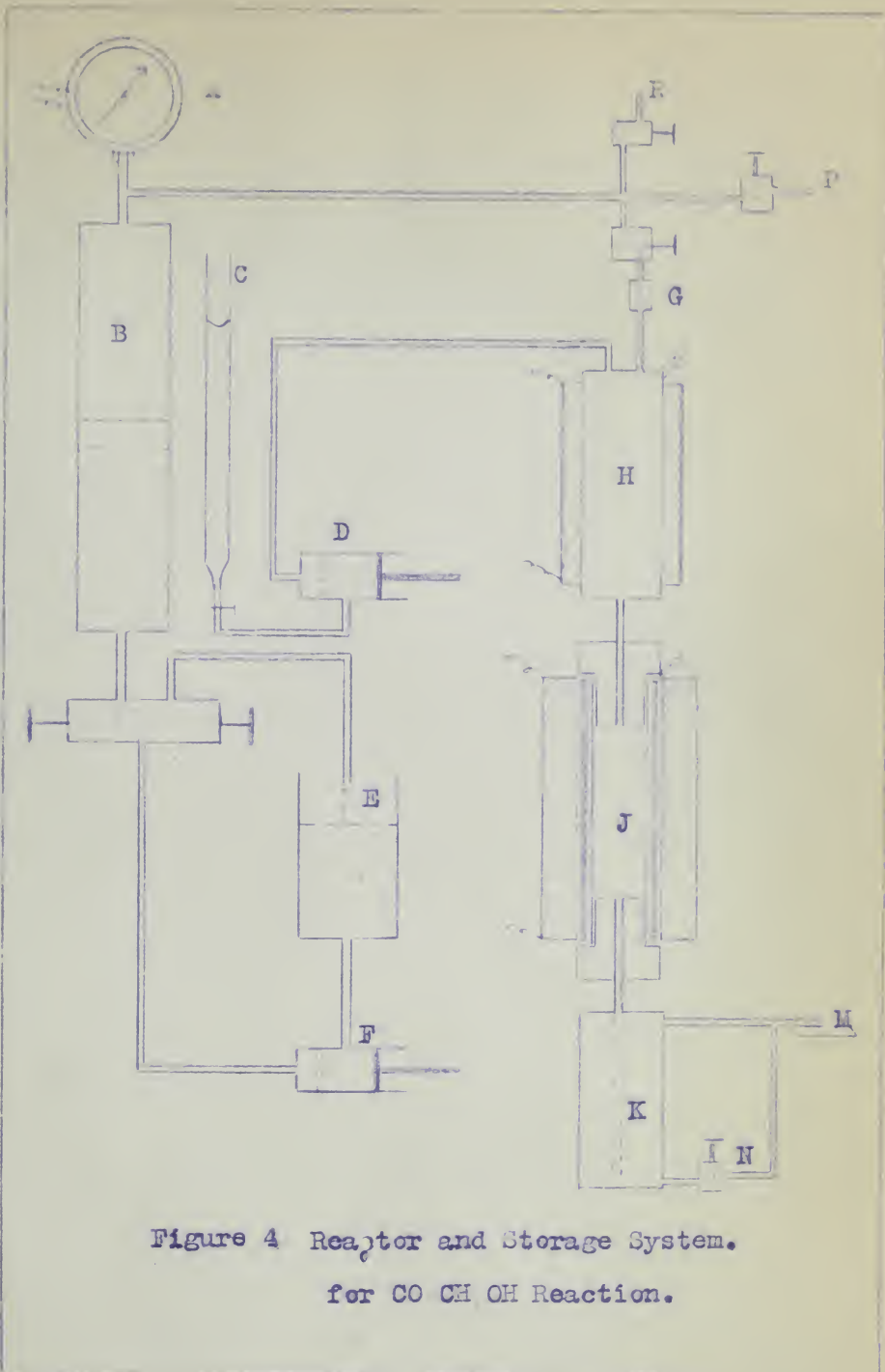
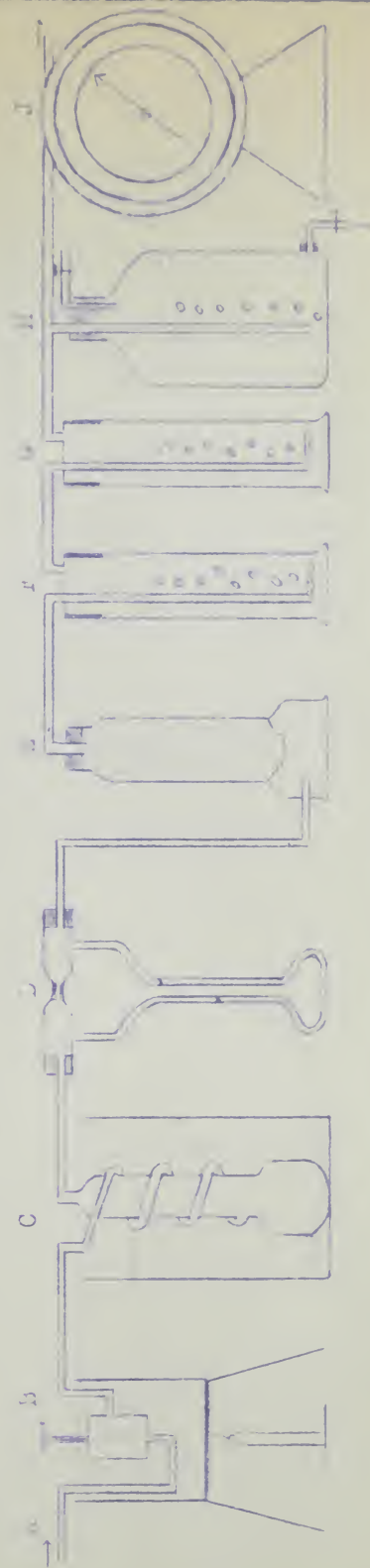Figure 4   Reactor and Storage System.

for CO CH OH Reaction.

Figure - Expansion Train for $CO + C_2OH$ Reaction.

Methanol from a 100 c.cm. burette C, could be pumped into the preheater by means of the adjustable stroke hydraulic pump D. The preheater was heated by means of resistance wire wound over asbestos sheet, sheathing the vessel. An outer layer of asbestos cement provided heat insulation. An iron-constantan thermocouple was soldered onto the preheater, beneath the asbestos sheet. During operation, the temperature of the preheater was maintained at $270^{\circ}C$ (30° above the critical temperature of methanol). It was controlled by rheostats in the heating circuit and a potentiometer recorder controller, to $\pm 2^{\circ}C$. The preheater was filled with copper turnings, to facilitate the mixing of the methanol vapours and the carbon monoxide. Blank runs showed that no chemical reaction took place in the preheater under these conditions.

From the preheater, the gases entered the reactor J. This reactor and furnace were the same as described in Part II. Briefly, the reactor consisted of a copper lined tube of high nickel chromium steel, of 30 c.cm. volume, maintained at the operating temperature by an automatically controlled electric furnace.

From the reactor, the off-gases and liquid products were led to the bottom of the bronze high pressure condenser K. This condenser was cooled in an ice-water mixture. The bulk of the unconverted methanol and other liquid products were condensed out here. The residual carbon monoxide and

other gaseous byproducts left the condenser through an over-
head take-off at M. The liquid products collected in this
condenser could be removed through the blow-off valve N.

Figure 5 shows the details of the expansion train.
It may be noted here that this train was used in both single
pass and circulation experiments. The off-gases from the
high pressure condenser were expanded to atmospheric pressure
through the heated expansion valve B. A spiral glass con-
denser C, maintained at $0^{o}C$ in an ice-water mixture, trapped
residual vapours in the off-gas. A flow meter D served to
indicate the rate of flow of off-gases from the system. A
calcium chloride drier, E, removed any uncondensed water and
methanol vapours from the gas. Fritted glass scrubbers,
E and F, were filled with concentrated sulfuric acid, and
removed dimethyl ether from the off-gas. A continuous pro-
portional gas sampler, indicated at H, followed the sulfuric
acid scrubbers. Readings on the wet-test meter J gave a
record of the off-gas volume. From this meter, the off-
gases were led to a water-sealed gas holder. This is not
shown in the figure.

It was found convenient to indicate the pumps D
and F in figure 4 as isolated pieces of equipment. Actually,
these pumps were mounted in the same block. They could be
operated independently of each other. The pumps were driven
by a small electric motor connected to a speed reducer. The
pump block, electric motor and speed reducer were mounted as

a unit on a heavy section of channel iron. This unit is
shown in the picture of the apparatus (figure 6).

The technique of operation of the expansion appa-
ratus was developed in several preliminary runs. First,
the catalyst was placed in the reactor. It was held in
position with several discs of copper gauze. The preheater
and reactor were next brought up to operating temperature.
During the heating period, the methanol feed line from the
pump D to the preheater was flushed with methanol, and
connected into the system. Simultaneously, the pressure of
carbon monoxide in storage vessel A was raised to the
desired operating value, by means of the pump F.

When these preliminary operations had been completed,
valve S was opened. This allowed carbon monoxide to enter
the preheater and reactor. The methanol pump D was then
started. The rate of delivery of the alcohol to the pre-
heater could be determined by observation of the liquid level
in burette C. This rate could be set within fairly wide
limits by the adjustment of the length of the piston stroke
in the pump. The rate of flow of carbon monoxide over the
catalyst was adjusted with the expansion valve B (figure 5).
This valve was set by reference to flow meter D.

At the end of a run, the methanol pump was stopped.
Valve R (figure 5) was closed, and the gases in the system
were allowed to escape into the expansion train. The liquid
products collected in the trap K were blown off into the glass
condenser by cautiously opening valve N.
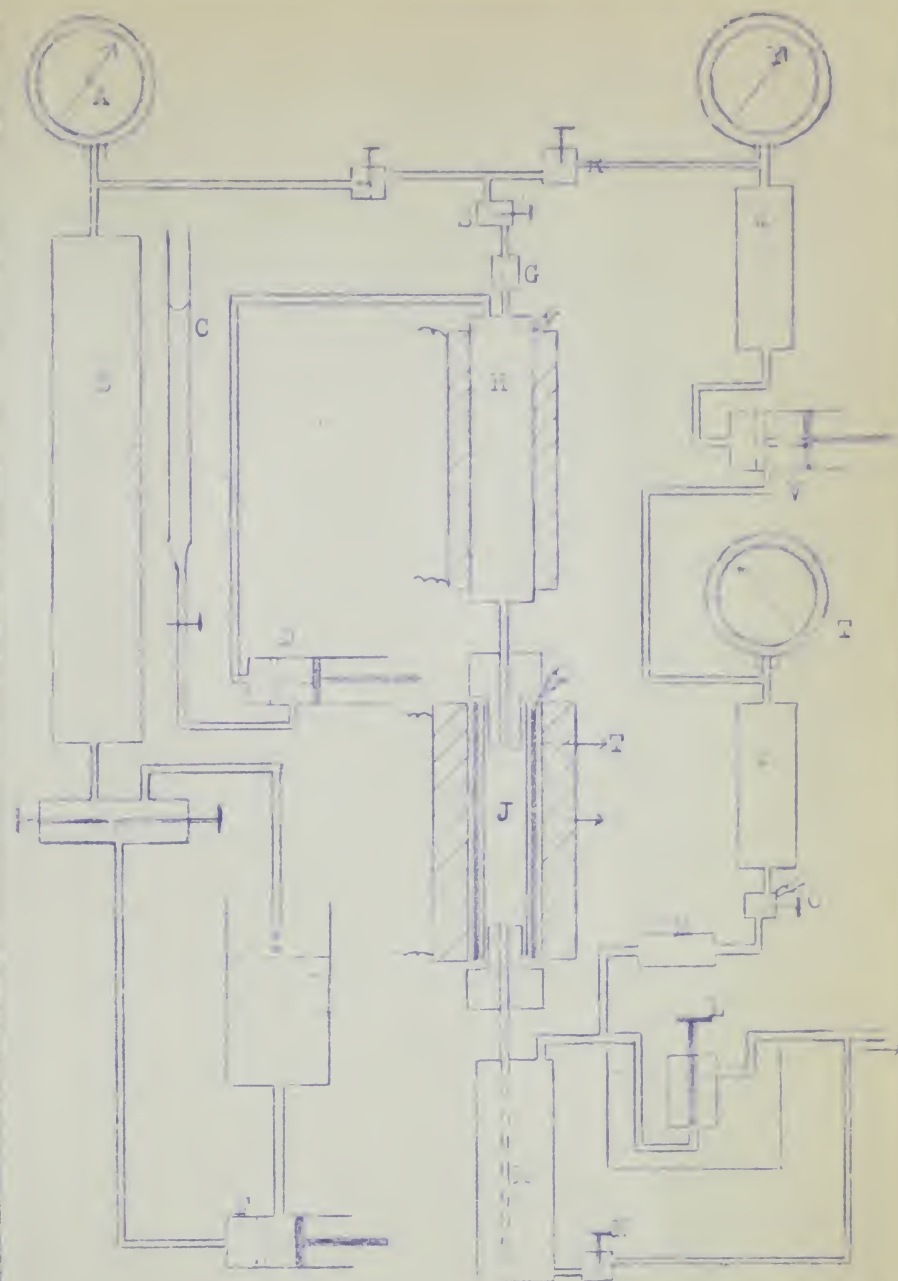
Figure 6. Hydraulic Pump Assembly.

Figure 7. Circulation Assembly for $CO-CH_3OH$
Reaction.

the suction side of the circulation pump, V, was indicated
by the Bourdon gauge T. From the circulation pump the gases
were compressed into another surge vessel W. The pressure
in this vessel was indicated by the Bourdon gauge Y. From
the pump, and surge vessel, the gas entered the preheater
again through valves R and S, and the check valve G.

The rate of circulation through this system could
be adjusted by variation of the suction pressure on the
pump V. An approximate determination of the circulation
rate was made with methane in place of carbon monoxide.
Methane under pressure was supplied from an auxiliary storage
system not shown in figure 7. This gas was expanded through
valve O, to a definite pressure, as indicated by the gauge
T, and then was compressed by the pump V to the operating
pressure to be used in experiments with carbon monoxide, as
indicated by gauge Y. From the delivery side of the pump,
the compressed methane was expanded to atmospheric pressure
through a heated expansion valve and a wet-test meter. By
a correlation of the volume of gas expanded through the
wet-test meter per minute, with the pressure on the suction
side of the pump, a calibration curve was drawn. It was
found that deviations of 50 p.s.i. in the suction pressure
were sufficient to change the rate of circulation consider-
ably. Pressure control was manual, and it was found possible
to reduce these variations to 25 p.s.i. Much wider variations
in the delivery pressure could be tolerated, changes as much

as 100 p.s.i. having little effect on the circulation rate.

Various procedures were followed in the operation of this apparatus. In run 59, after the preliminary operations described above for the single pass apparatus had been completed, pump V was started. Valve E, from carbon monoxide storage to the preheater was left open, and valve O, leading to the suction side of the circulation pump, was opened cautiously. Carbon monoxide from storage passed through the preheater, reactor and condenser to the circulation pump. The pressure on suction was kept at 300 p.s.i., and the pressure on the delivery side gradually built up. When the pressures indicated by gauges Y and T were the same, valve R was opened, and valve E was closed. The circulation system was then in operation as a unit, separate from the storage vessel B.

The methanol pump was then started. As the circulation continued, the pressure in the reactor, and on the delivery side of the pump V, as indicated by gauge Y, rose. This was due to gradual accumulation of dimethyl ether, methane and hydrogen in the circulating carbon monoxide. No fresh carbon monoxide was added during the run. At the conclusion of the experiment, the pumps D and V were stopped, and the gases were expanded at valve L into the expansion train previously described (figure 4). This procedure was, in effect, a type of static experiment. While circulation of gases over the catalyst was maintained, the carbon monoxide

consumed in formation of acetic acid, or in various side reactions possible, was not replenished.

In run 60, provision was made to enrich the circulating gases with carbon monoxide during operation. The preliminary operations were carried out as before. When the methanol pump had been started, and the gases were circulating through the apparatus, the expansion valve L (figure 7) was adjusted by reference to the flow meter in the expansion train. The rate of off-gas flow was such that a small pressure drop would occur during the run. At intervals, valve E, from the carbon monoxide storage was opened. The pressure in the circulation system immediately returned to the original operating values. In this way, the concentration of carbon monoxide in the gas stream was maintained.

Analytical Methods

Gas samples were collected over acidified sodium sulfate solutions, and analyzed as reported earlier.

Dimethyl ether was determined by absorption in concentrated sulfuric acid scrubbers. The off-gas was dried in a calcium chloride tower, and then passed through two fritted glass scrubbers in series. The gain in weight of the scrubbers was taken as dimethyl ether. The second scrubber was a guard. Any appreciable gain in weight in this scrubber was an indication that acid in the first scrubber had become nearly saturated with ether. This method was found quite satisfactory. The other constituents of the off-gas exhibited negligible solubility in sulfuric acid. In any case, the sulfuric acid soon became saturated with these other compounds while dimethyl ether was absorbed by chemical reaction. Sulfuric acid forms an addition compound with the ether.

Positive verification of the presence of dimethyl ether in the sulfuric acid was made in the following manner: the sulfuric acid containing the dissolved ether was allowed to drop into cold, saturated sodium sulfate solution. This dilution resulted in the evolution of a gas which was non-condensable in an ice-water mixture. The gaseous product was collected in a spiral glass condenser maintained at -36°C in a snow-sulfuric acid mixture. An approximate

determination of the boiling point of this liquid showed it
to be dimethyl ether.

The methods of analysis of the liquid products
varied somewhat, depending upon the nature of the catalyst.
In the case of neutral catalysts, as for example, calcium
phosphate, the products were weighed, made up to volume, and
aliquot portions taken for analysis. Free acid was deter-
mined first, by titration with standard 1.0N sodium
hydroxide. This free acid was considered to be acetic acid.
An excess of standard alkali was then added to the titrated
mixture, and any ester present was saponified by refluxing
for one hour. The loss of sodium hydroxide was then de-
termined by back titration with standard 1.0N sulfuric acid.
The results in these cases were expressed merely as total
acid. However, no separate estimation of ester was generally
made.

In the case of acid catalysts, no such direct
estimation of acetic acid was possible. The free acid in
the condensate was not only acetic acid, but the acid which
had been removed from the catalyst during the run and con-
densed out with the other liquid products. A method for
determination of acetic acid was developed which depended
upon the volatility of the acetic acid, and the non-
volatility of phosphoric acid.

An aliquot portion of the condensate was added to
15 c.c. of syrupy phosphoric acid. This mixture was distilled

until all volatile components had been removed. The con-
densate from this distillation contained water, acetic acid,
methanol, and methyl acetate. The amount of free acetic
acid was small, since the methanol and acetic acid in the
original aliquot were transformed into methyl acetate during
the distillation. The condensate was added to an excess of
standard 1.0N sodium hydroxide, and refluxed for one hour.
All the methyl acetate was saponified by this procedure,
with the consumption of an equivalent quantity of the
standard alkali. Back titration with standard 1.0N sulfuric
acid gave the volume of sodium hydroxide consumed in this
saponification reaction. This method did not permit separate
determination of methyl acetate. It was found by experiment
that phosphoric acid was non-volatile under these conditions.

The procedure was standardized by the use of
solutions of methanol, water, methyl acetate and acetic acid
made up gravimetrically. Recovery of acetic acid was found
to be complete with this method.

Positive identification of acetic acid was made by
conversion of a sample of the acid to the p-nitro benzyl
derivative, by treatment of the sodium salt with p-nitro
benzyl bromide. The resulting ester was recrystallized from
alcohol, and had a M.P. of 77-78°C as compared to 78°C re-
corded in the literature. This was considered conclusive
evidence that acetic acid was formed in this reaction.

Several runs were made with no catalyst in the

reactor. Condensates from these runs contained no titratable acid. This constituted a further check on the analytical procedure. If by any chance, formic acid were produced from decomposition of the methanol, it would be destroyed by dehydration to carbon monoxide and water during the distillation from phosphoric acid. It may be safely assumed then, that only acetic acid was assayed in this method.

In the circulation experiments, the contents of the potassium hydroxide high pressure scrubber had to be analyzed. At the conclusion of a run, the contents of this scrubber were added to a beaker of water, and the walls of the vessel were thoroughly flushed with water. This alkaline solution was evaporated to dryness in a drying oven. Such a procedure saponified any ester, and at the same time, removed all the water and alcohol. Acetic acid was retained as the non-volatile potassium salt. The residue was dissolved in water, and distilled from phosphoric acid as before. The condensate could be assayed by direct titration, since methanol was absent during the distillation step.

From time to time, various other tests of a qualitative nature were made. Thus, Schiff's fuchsin-aldehyde reagent was used in testing for aldehydes.

The burettes used in these determinations were calibrated. The standard solutions of sulfuric acid and sodium hydroxide were checked from time to time.

Experimental Results

The experimental results may be classified accord-
ing to the method used in the study of the reaction. The
results for the expansion method will be considered first.

A. Expansion Method.

The first runs were concerned mainly with the test-
ing of a group of miscellaneous catalysts. The results for
a representative group of experiments are given in Table IV.
It will be noted that conversion of methanol to acetic acid
was low with these catalysts. Relatively, much greater
amounts of alcohol were converted to dimethyl ether. No
reaction occurred in the absence of a catalyst (experiment
2). Even at 3500 p.s.i., (experiment 65) no carbonation of
methanol occurred. No side reactions were found. It is
evident that pressure alone is not sufficient to cause re-
action. A catalyst is required.

The results for catalyst 3B, (phosphoric acid and
copper phosphate) correspond to those obtained by Hardy[6].
He reported a 0.5% conversion per pass, using this same
catalyst. Results with catalyst 1B (calcium phosphate)
appear distinctly different from those obtained with other
catalysts. The low yield of dimethyl ether is interesting,
and the catalyst is worth further study. However, these
results may be dismissed without further discussion.

Catalyst 10B, phosphomolybdic acid on alumina,

TABLE IV

CO + CH₃OH REACTION

MISCELLANEOUS CATALYSTS

Run No.	2	4	7	21	24	27	28	67
Catalyst No.	None	1B	2B	7B	3B	8B	9B	Glass
Pressure, p.s.i.	1900	1800	2500	2000	1425	1950	2150	3500
Temperature, C.	360	360	400	350	400	360	360	360
Methanol to catalyst, grams	22.4	79.1	49.0	23.85	40.20	29.85	38.80	26.15
Off-gas Flow, L./minute	0.48	0.66	0.45	0.34	0.44	0.55	0.54	0.79
Volume off-gas, L. (N.T.P.)	32.4	74.3	56.7	23.4	29.0	47.8	54.9	52.8
Off-gas Analysis:								
CO₂ %	0.63	0.50	1.20	–	1.5	–	–	0.36
H₂	1.30	1.40	6.00	–	2.3	–	–	1.65
CO	98.1	93.15	93.0	–	89.4	–	–	96.28
CH₄	–	4.95	–	–	6.9	–	–	1.71
Condensate, grams	20.14	81.4	50.1	14.53	16.72	21.46	26.22	17.68
CH₃OH grams	20.14	80.6	49.2	12.75	15.09	18.47	23.67	17.55
CH₃COOH	0	0.80	0.72	0.42	0.27	0.25	0.33	0.03
H₂O	0	0.2	1.19	1.36	1.36	2.74	2.22	0.10
Dimethyl ether, grams	0.10	0.34	3.04	3.50	3.49	7.01	5.68	0.25
% Acid in condensate	0	1.0	1.4	2.9	1.6	1.2	1.2	0
% Methanol converted to:								
CH₃COOH	0	0.54	0.78	0.94	0.36	0.45	0.45	0
CH₃OCH₃	0	0.60	8.7	20.4	12.1	32.7	20.4	1.3

gave more promising yields of acetic acid. A series of
experiments were carried out with this catalyst in which the
effects of pressure, temperature and carbon monoxide:methanol
ratio on the yield of acetic acid were determined. The
results of these experiments are shown in Tables V, VI and
VII, and in figures 8 and 9.

The effect of pressure is shown in Table V, and
figure 8. The yield of acetic acid is increased from 2.2%
at 1300 p.s.i. to 4.1% at 2500 p.s.i. Pressure increments
above 2500 p.s.i. apparently do not increase the yield
(experiment 65). Dimethyl ether production remained roughly
constant at 43% for the range of pressures. At the higher
pressure, however, the catalyst was found to be badly
carbonized at the end of a run. Carbon dioxide was found to
extent of 7.1% in the off-gas at 3600 p.s.i., as compared
to 2.1% at 1300 p.s.i. This carbonization may be attributed
to the reaction

$$2CO \longrightarrow CO_2 + C$$

which is favoured by increased pressures. High pressures and
temperatures alone were not sufficient to cause this decom-
position. This is indicated in experiment 67 (Table IV),
carried out at 3500 p.s.i. and 360°C. No carbonization
occurred. This carbonization is known to be autocatalytic.
Since experiment 65 had been made with a partially carbonized
catalyst, a subsequent run was made with a new catalyst at
the same pressure and temperature. This run showed less

TABLE V

CO + CH₃OH REACTION

PHOSPHOMOLYBDIC ACID CATALYST (10B)

| Run No.	30	55	52	53	65
Pressure, p.s.i.	1300	1500	2000	2500	3600
Temperature, C.	360	360	360	360	360
Methanol to catalyst, grams	25.80	24.10	28.15	24.60	26.05
In-gas Analysis: %					
CO_2	—	—	—	—	0.40
H_2	—	—	—	—	2.05
CO	—	—	—	—	95.30
CH_4	—	—	—	—	2.25
Off-gas Flow, L./min.	0.75	0.59	0.60	0.61	0.71
Volume off-gas, L. a N.T.P.	76.4	52.0	54.7	43.2	70.0
Off-gas Analysis: %					
CO_2	2.06	—	—	—	7.13
H_2	4.41	—	—	—	6.12
CO	86.34	—	—	—	81.30
CH_4	7.19	—	—	—	5.45
Condensate, grams					
CH_3OH	17.93	9.38	13.01	9.69	10.00
CH_3COOH	13.99	4.92	8.22	4.63	5.09
H_2O	1.08	1.36	1.74	1.88	1.95
Dimethyl ether, grams	2.86	3.10	3.05	3.18	2.96
% Acid in Condensate	7.31	7.93	9.07	8.13	7.58
% Methanol converted to:	6.0	14.5	13.4	19.4	19.5
CH_3COOH	2.2	3.0	3.3	4.1	4.0
CH_3OCH_3	39.4	45.8	44.8	46.0	40.5
$CO:CH_3OH$ ratio	3:1	3:1	3:1	3:1	3:1
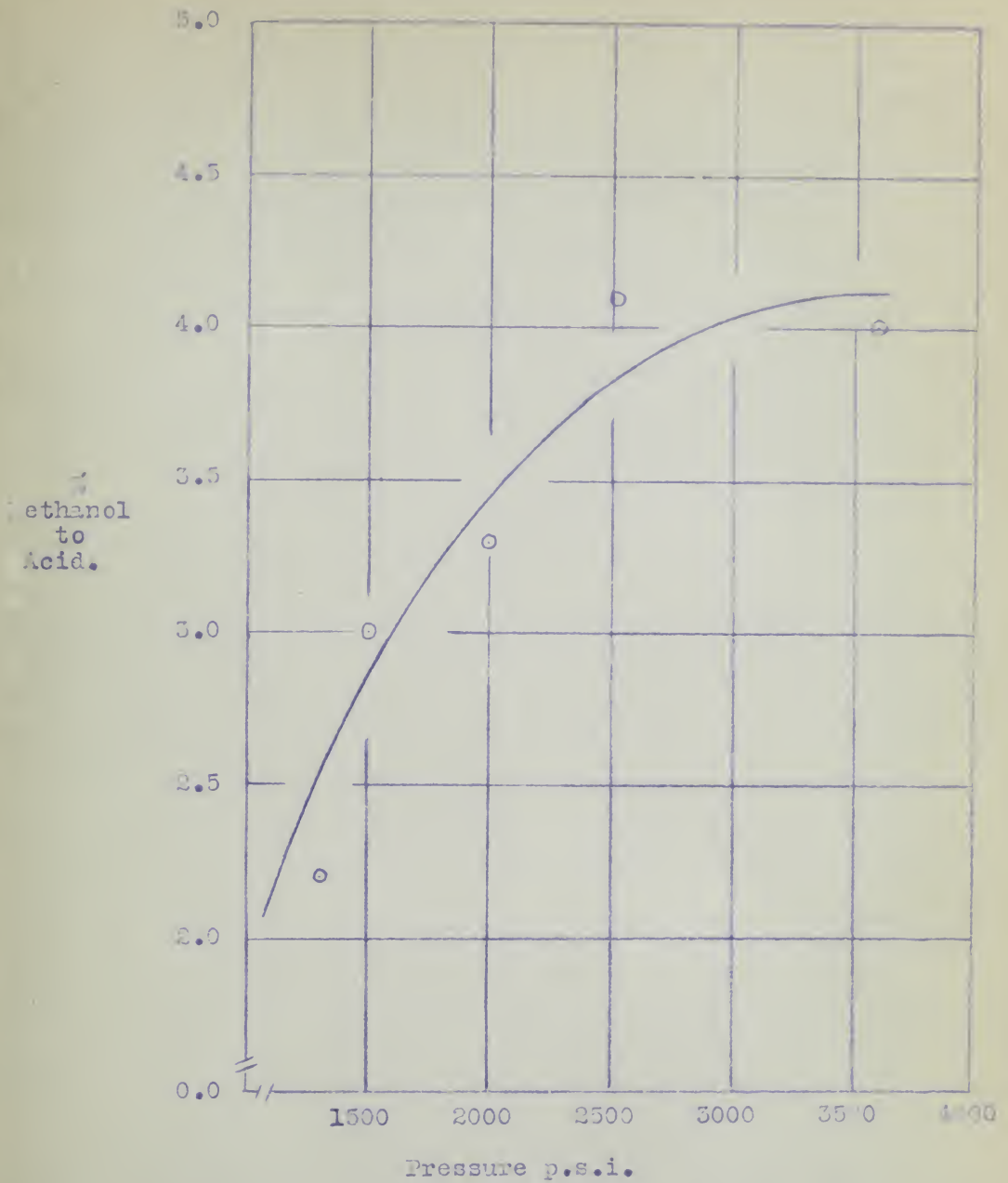
Figure 8. Yield of Acetic Acid at 360°C.

carbon dioxide in the off-gas (5.0%). It may be concluded
that while carbon monoxide by itself does not decompose
appreciably at 3500 p.s.i. and 360°C, this catalyst promotes
the reaction. Continued use of the catalyst accelerates
carbonization.

The effect of temperature on the reaction is in-
dicated in figure 9, and Table VI. Formation of acetic acid
is favoured by increased temperatures. The yield of acetic
acid is increased from 1.7% at 300°C to 3.3% at 390°C. At
the same time, dimethyl ether production passed through a
maximum at 360°C, reaching 45.8% (experiment 55). At 390°C,
ether formation dropped to 25.8%, while acetic acid produc-
tion rose to 3.3%. At this temperature, however, several
cubic centimeters of an oily product were found in the con-
densate. The nature of this product was not determined. At
the same time, the catalyst lost its activity to promote the
acetic acid reaction, as demonstrated in subsequent runs at
a lower temperature. Moreover, the off-gas contained 9.8%
methane, indicating thermal decomposition of dimethyl ether.
Oil formation may be ascribed tentatively to the same re-
action.

Formation of acetic acid by this reaction is
influenced by the ratio of carbon monoxide to methanol in
the gas stream. Table VII shows the effect of this factor.
Higher yields of acetic acid were obtained at the 3:1 ratio
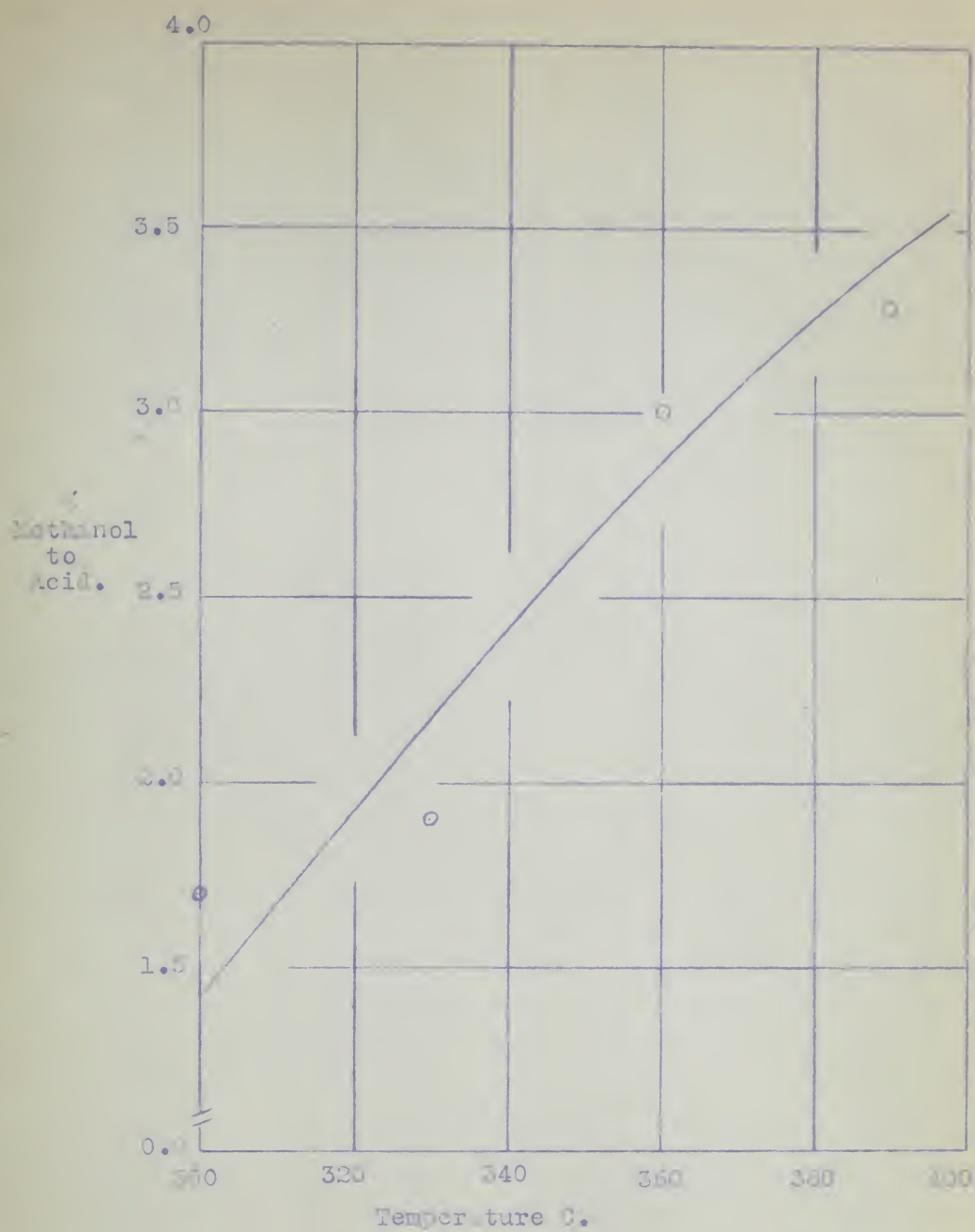(experiments 63 and 53) than at the 1:1 ratio (experiments

Figure 9. Yield of Acetic Acid at 1500 p.s.i.

TABLE VI

CO + CH₃OH REACTION

PHOSPHOMOLYBDIC ACID CATALYST (10B)

Run No.	55	61	62	63
Pressure, p.s.i.	1500	1500	1500	1500
Temperature, C.	360	300	330	390
Methanol to catalyst, grams	24.10	27.45	24.45	27.40
In-gas Analysis:				
CO_2 %	-	0.0	0.0	0.10
H_2	-	6.3	6.3	1.29
CO	-	88.4	88.4	98.6
CH_4	-	5.3	5.3	0.0
Off-gas flow, L./min.	0.59	0.83	0.65	0.67
Volume off-gas, L. a N.T.P.	52.0	56.1	48.5	60.6
Off-gas Analysis:				
CO_2 %	-	2.22	3.2	6.7
H_2	-	5.34	6.4	8.56
CO	-	88.21	84.3	74.97
CH_4	-	4.23	6.1	9.77
Condensate, grams	9.38	19.95	13.74	13.71
CH_3OH	4.92	16.98	9.84	10.04*
CH_3COOH	1.36	0.85	0.86	1.69
H_2O	3.10	2.12	3.04	1.98
Dimethyl ether, grams	7.93	5.43	7.72	5.08
% Acid in Condensate	14.5	4.3	6.3	12.3
% Methanol converted to:				
CH_3COOH	3.0	1.7	1.9	3.3
CH_3OCH_3	45.8	27.6	44.0	25.8
$CO:CH_3OH$ ratio	3:1	3:1	3:1	3:1

* 2.0 c.cm. oil included in this figure.

TABLE VII

CO + CH3OH REACTION

PHOSPHOMOLYBDIC ACID CATALYST (10B)

| Run No.	56	46	54	55	53
Temperature, C.	360	360	360	360	360
Pressure, p.s.i.	1500	1500	2500	1500	2500
Methanol to catalyst, grams	17.60	41.60	26.40	24.10	24.60
Off-gas Flow L./min.	0.65	0.30	0.30	0.59	0.61
Volume off-gas L. a N.T.P.	62.6	29.0	22.8	52.0	43.2
Condensate, grams	6.01	27.01	9.22	9.38	9.69
CH3OH	2.73	22.21	4.95	4.92	4.63
CH3COOH	0.98	0.93	1.37	1.36	1.88
H2O	2.30	3.87	2.90	3.10	3.18
Dimethyl ether, grams	5.89	9.90	7.66	7.93	8.13
% Acid in Condensate	16.3	4.2	14.9	14.5	19.4
% Methanol converted to:					
CH3COOH	3.0	1.2	2.8	3.0	4.1
CH3OCH3	46.6	33.2	40.4	45.8	46.0
CO:CH3OH ratio	5:1	1:1	1:1	3:1	3:1

46 and 54). However, increasing the ratio to 5:1 (experiment 56) did not change the yield of acid from that obtained at 3:1 ratio. Lower yields of ether were encountered at the 1:1 ratio.
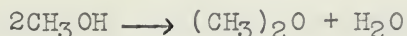
Dimethyl Ether Formation -

It has been suggested by Sabatier (16) that methyl acetate decomposes over metallic oxides to form dimethyl ether. The mechanism he suggests is as follows:

$$MO + 2CH_3COOCH_3 \longrightarrow (CH_3CO)_2O + (CH_3O)_2M$$

$$(CH_3O)_2M \longrightarrow (CH_3)_2O + MO$$

$$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3COOH$$
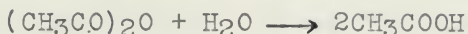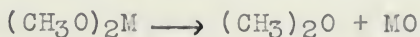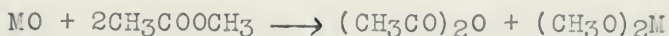
MO being a metallic or basic oxide. The net effect of these consecutive reactions is

$$2CH_3COOCH_3 + H_2O \longrightarrow 2CH_3COOH + (CH_3)_2O$$
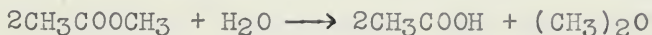
The carrier for catalyst 10B was a metallic oxide, alumina. Methyl acetate has been demonstrated in the liquid products in many of these experiments, and no doubt was formed by vapor phase esterification of acetic acid with the excess methanol present. If the reaction suggested by Sabatier occurred to any extent in this work, then dimethyl ether formation would be a measure of original acid production. The concurrent reaction

$$2CH_3OH \longrightarrow (CH_3)_2O + H_2O$$

would, of course, also account for dimethyl ether formation.

Fortunately, both of these possibilities were subject to experimental confirmation. Accordingly a run was

made in which pure methyl acetate replaced methanol, and
methane replaced carbon monoxide. It was found that methyl
acetate did undergo decomposition to dimethyl ether to extent
of 13.4%. A corresponding amount of free acid was formed.
In this experiment, conditions of pressure, temperature and
space velocity were of the same order as those used in
experiments with carbon monoxide and methanol. Thus at a
temperature of 360°C and pressure of 1500 p.s.i. of methane,
32.15 grams of methyl acetate produced 1.83 grams of dimethyl
ether and 6.76 grams of acetic acid. The residual ester
remained unconverted. It may be concluded that while some
dimethyl ether may be formed by this reaction, other re-
actions must account for the principal production.

A series of experiments were now carried out to
investigate the concurrent reaction

$$2CH_3OH \longrightarrow (CH_3)_2O + H_2O$$

Here again methane was used as a carrier. The results of
these experiments are shown in Table VIII and figure 10.

From these experiments, it is evident that dimethyl
ether formation may be accounted for solely by independent
dehydration of methanol. The effect of water on the de-
hydration of methanol is shown in figure 10. At 360°C, as
the concentration of methanol in aqueous solution decreased
from 100% to 70%, the conversion of alcohol to ether dropped
from 45.7% to 14.5%. At 400°C, corresponding figures for
ether formation were 42.1% and 29.4% respectively.

TABLE VIII

FORMATION OF CH3OCH3 FROM CH3OH OVER CATALYST 10B

| Run No.	37	38	39	40	41	43	44
Pressure, p.s.i.	800	750	750	1100	1100	900	800
Temperature, C.	360	360	360	400	400	400	400
% Methanol in aqueous solution	100	85	70	70	100	100	85
Methanol solution to catalyst, grams	32.75	35.65	39.20	39.90	31.60	36.50	33.85
Off-gas Flow, L./min.	0.77	0.78	0.79	0.77	0.73	0.73	0.75
Off-gas Volume, L./N.T.P.	49.5	52.3	46.7	62.3	44.8	49.9	47.2
Condensate, grams	15.78	23.65	34.67	23.83	12.71	13.49	19.44
Dimethyl ether, grams	10.73	5.84	2.86	5.92	9.55	10.48	7.87
% Methanol converted to CH3OCH3	45.7	26.8	14.5	29.4	42.1	40.0	38.0
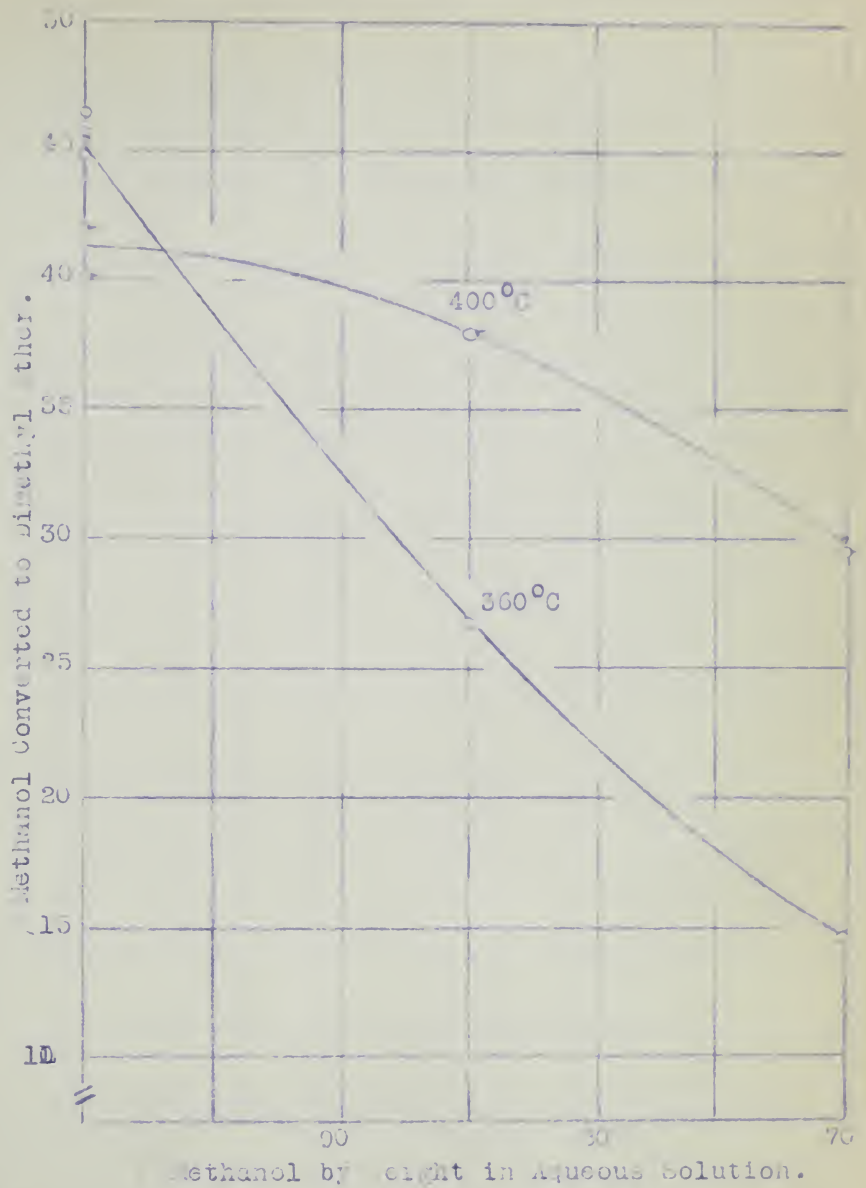
Figure 10. The Effect of Water on the Conversion
of Methanol to Dimethyl Ether.

These results suggest that an equilibrium

$$2CH_3OH \rightleftarrows (CH_3)_2O + H_2O$$
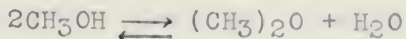
was established over the catalyst. As water was added to methanol, the equilibrium shifted to the left. Addition of water to methanol may be regarded as a means of suppressing this undesirable side reaction in the formation of acetic acid from methanol and carbon monoxide.

Hardy[6], and Singh and Krase[9], as noted earlier, have suggested that dimethyl ether is an intermediate in the formation of acetic acid by this reaction. This of course implies that formation of dimethyl ether from alcohol occurs first, followed by the reaction of carbon monoxide with the ether thus formed, to produce acetic acid. The experiments outlined in Table IV do not indicate any such relationship. Comparing the data in Tables IV and V, a general increase in acid production is accompanied by a corresponding increase in ether production, suggesting ether as an intermediate. Chemically, such a reaction does not seem probable. Independent reactions appear more likely to the writer.

Methane and Hydrogen Formation -

From the point of view of production of acetic acid from methanol, formation of dimethyl ether is undesirable. However, the dehydration reaction has been shown to be reversible, and under suitable conditions, dimethyl ether may be reconverted to methanol[20]. Moreover, dimethyl ether has commercial uses in its own right. Conversion of

methanol to hydrogen and methane is another matter. Such a reaction represents permanent conversion of the alcohol to a waste product.

Except in a few instances, quantitative results relating to this side reaction cannot be deduced from the data obtained in this work. In general, it was not found practicable with the apparatus available to determine the composition of the in-gas. However, certain statements can be made. Comparing results of experiments 65 and 62 (Tables V and VI respectively) it is seen that increased pressures reduce the formation of methane and hydrogen. Also, high temperatures favour the formation of these by-products. This is exemplified in experiment 63, carried out at 1500 p.s.i. and 390°C, where methane and hydrogen appeared in the off-gas to the extent of 9.8% and 8.6% respectively. Experiment 61, carried out at 1500 p.s.i. and 300°C, showed 4.2% methane and 5.3% hydrogen. In-gas analyses were made in these cases and make the comparison valid.

The transformation of alcohol to methane and hydrogen may be explained in various ways. Hinshelwood and Askey[7] found that dimethyl ether readily underwent decomposition to methane and hydrogen according to

$$CH_3OCH_3 \longrightarrow (HCHO) + CH_4$$
$$(HCHO) \longrightarrow CO + H_2$$
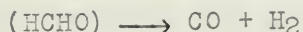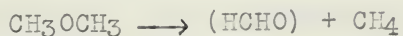
Formaldehyde was found to be an unstable intermediate in the decomposition reaction. The consecutive reactions

$$CH_3OH \longrightarrow CO + 2H_2$$
$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$
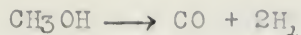
are another possible source of these products. However, catalysts possessing the characteristics of alumina are unlikely to promote the hydrogenation reaction required.

B. Circulation Method.

From the results obtained in the expansion method, it has been seen that formation of dimethyl ether and associated products was several times that of acetic acid. Under optimum conditions for the one pass system, 4.1% of the methanol was converted to acetic acid, while 45% was converted to dimethyl ether. Smaller but significant amounts were converted to methane and hydrogen. By recirculation of these gaseous by-products over the catalyst, it was hoped that side reactions would be suppressed, and yields of acetic acid would be increased.

As has been mentioned earlier, the apparatus available for this type of experiment was rather limited. However, sufficient data has been obtained to allow certain conclusions to be drawn. The results of these experiments are shown in Table IX.

The methods used in these experiments have been outlined previously. In experiment 59, it was found that dimethyl ether formation was reduced to 38.2%. Acetic acid production remained at 4.0%. However, methane and hydrogen production increased greatly, being 11.6% and 7.4% respectively. This suggests that recirculation of the off-gas

TABLE IX

$CO + CH_3OH$ REACTION

CIRCULATION METHOD

Run No.	59	60
Temperature, C.	360	360
Pressure, p.s.i.	1840	2000
Methanol to catalyst, grams	44.10	22.95
Rate of Circulation, L./min.	7.1	7.1
Gas Analysis:		
CO_2 %	0.0	0.0
H_2	6.3	6.3
CO	88.4	88.4
CH_4	5.3	5.3
Volume off-gas, L./at N.T.P.	49.0	50.0
Off-gas Analysis:		
CO_2 %	3.89	3.14
H_2	7.42	5.80
CO	77.08	84.15
CH_4	11.61	6.80
Condensate, grams	27.57	13.76
CH_3OH	19.51	9.93
CH_3COOH	3.29	1.58
H_2O	4.77	2.25
Dimethyl ether, grams	12.21	5.77
% Acid in Condensate	11.9	11.5
% Methanol converted to		
CH_3COOH	4.0	3.7
CH_3OCH_3	38.2	35.1

over this catalyst permits catalytic decomposition of dimethyl ether to methane and hydrogen. Thus on recirculation, the dimethyl ether-methanol-water equilibrium would not be established until methane and hydrogen concentrations had reached values sufficiently high to suppress further ether decomposition. The partial pressure of carbon monoxide is decreased by these concurrent reactions. This, of course, would have a deleterious effect on carbonation of methanol. From the data of Table IX, one cannot say whether or not these equilibria have been reached. However, the increased survival of methanol in the liquid products, 44.3% in experiment 59, and 43.3% in experiment 60, as compared to 19.0% in experiment 53, indicate that equilibrium between methanol and methyl ether has been approached.

The results of experiment 60 were analogous to those obtained in experiment 59. Higher concentration of carbon monoxide in the circulating gas was obtained by a continuous purge of gas into the expansion train, together with addition of carbon monoxide-rich gas at intervals. Such a procedure did not change the yield of acetic acid appreciably, 3.7% of the methanol being so converted. 35.1% of the alcohol was converted to dimethyl ether. Concentration of methane and hydrogen in the off-gas was found to be somewhat lower than in run 59. This was to be expected from the continuous addition of carbon monoxide and the continuous removal of products. These experiments were not particularly

well-controlled, but increased survival of methanol indicates
the desirability of further improved experiments.

Discussion of Results

In the previous section, the results have been pre-
sented, together with a discussion of the salient points.
With a phosphomolybdic acid catalyst, (10B), it has been
found that yield of acetic acid from carbonation of methanol
was a function of the pressure, temperature, and to a lesser
extent, the carbon monoxide:methanol ratio. The upper limit
of pressure has been reached at 3600 p.s.i. Over catalyst
10B at this pressure, deposition of carbon became excessive.
In addition, yield of acetic acid was found to be unchanged
from that obtained at 2500 p.s.i.

Formation of acetic acid increased with the tempera-
ture. However, temperatures of 400°C and beyond decreased
the life of the catalyst. At 360°C, the catalyst retained
its activity for longer periods. Oil formation at the higher
temperatures probably caused this loss of activity.

Carbonation of methanol over phosphomolybdic acid
was accompanied by several side reactions, notably dimethyl
ether formation and conversion of alcohol to hydrogen and
methane. Variations in pressure had but little effect on
ether formation. Variations in temperature were found to
exert a greater effect, maximum production being found at
360°C. It was found that methyl acetate was unstable with
respect to dimethyl ether. However, dehydration of methanol

probably accounted for the major proportion of dimethyl ether.
This side reaction could be suppressed by the addition of
water to methanol. Recirculation of off-gases reduced ether
formation by about 15%. Even under optimum conditions, the
ratio of ether to acetic acid in the products was high,
being 10:1.

Methane and hydrogen formation was also found to be
a function of pressure and temperature. Production of these
gases increased with temperature, and decreased with increased
pressure. These results are to be expected from Le Chatelier's
principle.

Recirculation of off-gases had little effect on the
yield of acetic acid. However, it was found that yields
obtained at 2500 p.s.i. in expansion experiments could be
obtained at 1850 p.s.i. in recirculation experiments. Sur-
vival of methanol in the liquid products was increased by
recirculation. This factor would be of some importance in
successful industrial application of the method.

Increased survival of methanol for the same yield
of acetic acid is indicative of suppressed side reactions,
and represents increased yields of acid based on consumption
of alcohol. These side reactions must be suppressed still
further if economic operation of such a process is to be
considered. A catalyst possessing more selective action for
the carbonation reaction is desirable. Further investiga-
tions would involve an examination of less active carriers

for the catalyst, as for example, silica gel, porcelain, or pumice stone. These materials would not, in all probability, have such a strong dehydrating action on methanol, while at the same time, they possess the required mechanical characteristics of a good carrier.

GENERAL SUMMARY

The possibility of direct catalytic carbonation of methane to acetic acid has been investigated over a wide range of temperatures and pressures. Such a possibility, confirming thermodynamic calculations, was found to be remote. No acetic acid was found.

The nature of the reactions among oxygen, methane and carbon monoxide over a copper catalyst has been investigated. Oxidation of carbon monoxide was found to be the predominant reaction. Methane remained unoxidized until its partial pressure was seventeenfold that of carbon monoxide. No evidence was obtained that acetic acid could be produced by the consecutive oxidation and carbonation of methane to methanol and acid respectively.

The catalytic preparation of acetic acid from methanol and carbon monoxide has been investigated. The largest yields of acetic acid were obtained with a phospho-molybdic acid catalyst. The effect of temperature and pressure on yield of acetic acid has been ascertained, maximum conversion occurring at 360°C and 2500 p.s.i. Condensates containing 19.5% acetic acid were obtained under optimum conditions. Conversion of alcohol to methyl ether could be suppressed by use of aqueous methanol, and to a lesser extent, by recirculation of off-gases over the catalyst.

Several possible mechanisms for the production of
these compounds were investigated. Independent dehydration
of methanol to methyl ether was found to offer a complete
explanation for the formation of these by-products. Theories
developed by other workers requiring dimethyl ether as an
intermediate in the formation of acetic acid could not be
confirmed.

BIBLIOGRAPHY

1. Betts, R. H., Chemistry 110 report, Dept. of Chemistry, University of Alberta (1942).

2. Boomer, E. H., and Thomas, V., Can. J. Research, B, 15:414 (1937).

3. Dreyfus, French Pat., 768, 584 and British Pat., 226, 248.

4. Gillies, A., and Hugill, J. T. Thesis, University of Alberta Library (1940).

5. Grignard, V., Ann. Chim. Phys. (7), 24, 433 (1901).

6. Hardy, D. V. N., J. C. S., 1335 (1936).

7. Hinshelwood, C. N., and Askey, P. J., Proc. Roy. Soc. (London) 115 A, 215 (1927).

8. Hurd, C. D., and Martin, K. E., J. A. C. S., 51, 3614 (1929).

9. Krase, N. W., and Singh, A. D., I. E. C., 27, 909 (1935).

10. Merrill, D. R., and Scalione, C. C., J. A. C. S., 43, 1987 (1921).

11. Maldowski, B., J. Applied Chem., U.S.S.R., 4, 667 (1931).

12. Morris, H. E., Thesis, University of Alberta Library (1931).

13. Naldrett, S. N., Thesis, University of Alberta Library (1938).

14. Nef, J. U., Ann., 318, 221 (1901).

15. Parks, G. S., and Huffman, H. M., The Free Energies of Some Organic Compounds - Reinhold Publishing Corp., 1932.

16. Sabatier, P., and Mailhe, A., Compt. rend., 152, 669 (1912) and 154, 49 and 175 (1912).

17. Sabatier, P., and Senderens, J. B., Chim. Phys., (8) 4 467 (1905).

18. Thacker, C. M., Folkins, H. O., and Miller, E. L., I.E.C., 33, 587 (1941).

19. Thomas, V., Thesis, University of Alberta Library (1936).

20. Whitmore, F. C., Organic Chemistry, Page 150. D. Van Nostrand Co. (1937).